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CONTENTS

RP. No.	TITLE AND AUTHOR	Page
630.	Development of standard-frequency transmitting sets. L. Mickey and A. D. Martin	1
631.	Data on the spectral erythemic reaction of the untanned human skin to ultraviolet radiation. W. W. Coblentz and R. Stair	13
632.	Studies of the ionosphere and their application to radio transmission. S. S. Kirby, L. V. Berkner, and D. M. Stuart	15
633.	Reactions of lithographic papers to variations in humidity and temperature. C. G. Weber and L. W. Snyder	53
634.	A glass electrode potentiometer system for the determination of the pH values of weakly buffered solutions such as natural and treated waters. John O. Burton, Harry Matheson, and S. F. Acree	67
635.	Analysis of wool-cotton textiles. Ralph T. Mease and Daniel A. Jessup	75
636.	A new cathode-ray oscillograph and its application to the study of power loss in dielectric materials. Forest K. Harris	87
637.	Influence of neighboring structures on the wind pressure on tall buildings. C. L. Harris	103
638.	Soil corrosion studies, 1932. Rates of loss of weight and pitting of ferrous and nonferrous specimens and metallic protective coatings. K. H. Logan and R. H. Taylor	119

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BUREAU OF STANDARDS JOURNAL OF RESEARCH

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U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP630

Part of Bureau of Standards Journal of Research, vol. 12, January 1934

DEVELOPMENT OF STANDARD-FREQUENCY TRANSMITTING SETS

By L. Mickey and A. D. Martin

ABSTRACT

This paper describes the development of radio transmitting equipment used in the standard-frequency service provided by the Bureau since 1923. Difficulties encountered in the design and operation are discussed and improvements noted. In the establishment of the 5,000 kc/s schedules, innovations in frequency multiplication and control, based on the principle of the synchronized oscillator and harmonic amplifier, are described. Expansion of the transmitting equipment to the present 30-kw installation is covered in detail. Diagrams and photographs of the Beltsville, Md., transmitting station are given.

CONTENTS

		Page
I.	Introduction	1
II.	Early standard-frequency transmitters	2
III.	Changing demands of the service	3
IV.	Choice of frequency	3
V.	Synchronized oscillators	3
VI.	Harmonic amplifiers	6
VII.	30-kw transmitter	7
VIII.	Results	11

I. INTRODUCTION

The widespread development of radio has brought increasing demand for close regulation of all radio frequencies to insure the maximum utilization of the available spectrum. In order to comply with governmental regulations, which become more and more exacting, each radio station must have access in some form to an accurate standard of frequency. This may be an independent standard of high accuracy, a substandard periodically compared by wire or radio with a precision standard, or a frequency supplied continuously by radio or wire from a precision standard.

National standards of frequency are maintained by the government laboratories of the various nations as bases of frequency assignment and administration. Comparisons with the national frequency standards are accomplished through three principal activities of the government laboratories: (1) Measurement of station frequencies; (2) measurement and calibration of frequency meters, piezoelectric oscillators, and other standards sent to the laboratory for that purpose, and (3) the radio transmission of standard-frequency signals. The first method becomes a large and expensive undertaking while the second is subject to inaccuracies resulting from changes of instruments in transit. Consequently, the third method of comparison has become increasingly important. It has proved to be the most accurate, economical, and practical means of dissemination of the national frequency standard.

A radio transmission of standard frequency may consist of: (*a*) A standard radio-frequency signal, (*b*) a radio-frequency carrier modulated by a standard audio frequency, or (*c*) a standard radio-frequency carrier modulated by a standard audio frequency. In Europe, the Laboratoire National de Radioelectricité and the National Physical Laboratory use a standard frequency of 1 kc/s to modulate a carrier frequency of approximately 200 kc/s. As in (*b*) above, the accuracy of the carrier frequency is not held to be of major importance. The practice in the United States has been the transmission of unmodulated standard radio-frequency signals, although experimental transmissions of the (*c*) classification are being conducted. Since early in 1923 the Bureau of Standards has provided a service of transmitting standard-frequency signals which at various times have covered the range from 125 to 10,000 kc/s.

II. EARLY STANDARD-FREQUENCY TRANSMITTERS

The first apparatus used for the transmission of standard frequencies consisted of a single self-excited triode oscillator coupled to a simple antenna. It was adjusted to the desired frequency by means of a precision frequency meter. A stage of power amplification was later added for the purpose of minimizing the effects of varying antenna characteristics as well as increasing the distance range of transmission.

The development of the piezoelectric frequency standard provided a great improvement in the accuracy of the transmissions. Schedules were arranged so that all transmitted frequencies were multiples of a 100- or 200-kc/s standard. The oscillator was adjusted to the desired frequency by the method of beats between the transmitter and harmonics of the standard. A fine adjustment of the circuit capacitance made possible an accurate frequency setting.

Two transmitters were employed to cover approximately 30 frequencies between 125 and 6,000 kc/s. Numerous difficulties limited the accuracy attainable. Poor regulation of power supply and temperature changes in tube and circuit elements caused some shifting of frequency. Furthermore, the wide range of frequencies made difficult the neutralization of the power amplifier.

Greater need for the service on the higher frequencies and the impracticability of transmissions within the broadcast band because of interference from the numerous stations of greater power, resulted in a shifting of the schedule to the range from 1,500 to 10,000 kc/s. In 1930 one transmitter was dismantled and the other reconstructed for more efficient operation on the higher frequencies. An improved type of oscillator tube and a 500-watt screen-grid power amplifier tube were installed. Oscillator inductors of heavy copper tubing were constructed, forced ventilation was applied, and an adequate power supply and filter system were provided. A variable-length, single-wire, voltage-fed antenna was employed. The length was adjusted to the optimum value for each operating frequency. A view of this transmitter is shown in figure 1.

While this equipment showed much improvement over the earlier, several limitations remained. Temperature changes in the oscillator, with the consequent frequency variations, persisted in spite of the improved ventilation. These were caused mainly by the large radio-frequency currents and the use of changeable inductors. In this connection many desirable changes suggested themselves. These

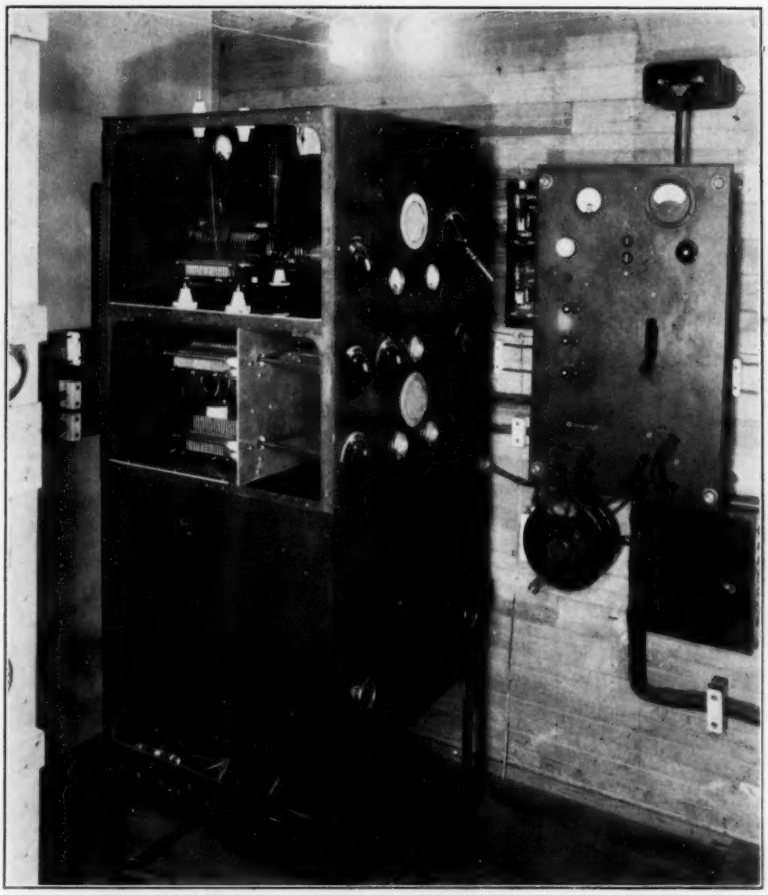

FIGURE 1.—*Early standard-frequency transmitter—1,500 to 10,000 kc/s.*
Multiplier-amplifier oscillator systems.

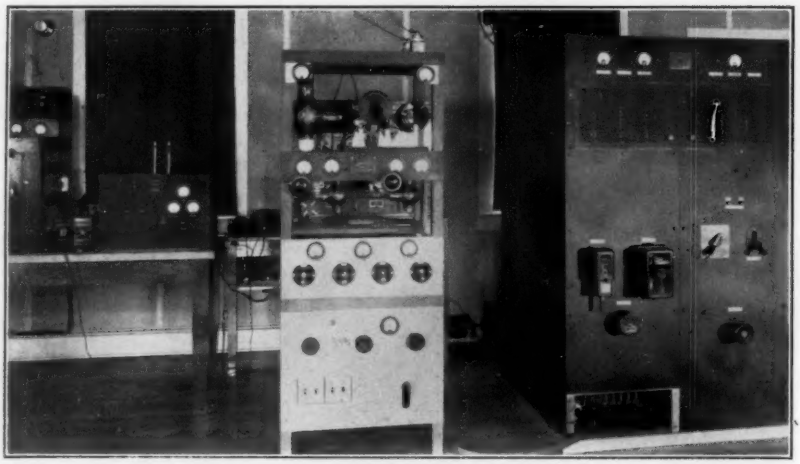

FIGURE 3.—*1-kw experimental 5,000-kc/s transmitter with rectifier.*

included the reduction of the oscillator power and the installation of intermediate screen-grid amplifiers to minimize the effects of all external influences on the oscillator, the use of continuously variable inductors throughout the transmitter, and, finally, an increase in power output to provide better distance coverage. This type of transmitter was abandoned, however, in favor of equipment with more elaborate and dependable frequency control.

III. CHANGING DEMANDS OF THE SERVICE

The service heretofore described made a number of frequencies conveniently available through the greater part of the radio frequency spectrum. With the growth of large communication systems, there has been a development of elaborate working standards and monitoring stations whereby all radio stations in a system have their frequencies accurately checked. In addition, several commercial organizations offer a general frequency-monitoring service. Broadcasting stations are required by law to have accurate frequency-monitoring equipment. The American Radio Relay League conducts a schedule of standard-frequency transmissions which serves the amateur bands. The Federal Radio Commission maintains a number of monitoring stations for the careful checking of all station frequencies. There has thus been a change in the type of service demanded from an extensive range of standard frequencies formerly provided to a basic frequency of extreme accuracy directly controlled by the national frequency standard. Such a single frequency makes available a direct, convenient, and accurate comparison with the national standard to every radio inspector, communication company, manufacturer of frequency standards and control units, scientific laboratory, amateur, or other interested party.

IV. CHOICE OF FREQUENCY

With this fact in mind, efforts were made to determine a suitable single radio frequency for the purpose. The advantages of a low or medium frequency were more than offset by the cost of the required installation, while broadcast frequencies were undesirable for obvious reasons. The choice, therefore, lay in the region above 1,500 kc/s. A study of transmission phenomena for day and night, winter and summer conditions showed that no single frequency would actually give universally satisfactory service. A frequency of 5,000 kc/s was chosen as the best compromise value, because of its usual lack of skip distance and yet its comparatively wide coverage, its relative freedom from interference with previously assigned stations, and its convenient integral relation with most frequency standards. The harmonic frequencies of 10,000, 15,000, and 20,000 kc/s were also chosen for future experimental purposes.

V. SYNCHRONIZED OSCILLATORS

The national primary standard of frequency maintained by the Bureau consists of a group of 100- and 200-kc/s piezo oscillators [1] which are compared daily with the Naval Observatory time signals.

[1] A high precision standard of frequemcy. W. A. Marrison. Proc. I.R.E., vol. 17, p. 1103, July 1929. Bell System Tech. Jour., vol. 8, p. 493, July 1929; The accuracy of the primary frequency standard of the Bureau of Standards. C. G. McIlwraith. Trans. Am. Geophysical Union, Twelfth Annual Meeting (Ntl. Acad. Sci., Washington, D.C.), p. 29, 1931.

The direct control of the transmitted frequency by the standard presented the problem of multiplying the standard frequency of 100 or 200 kc/s to the desired 5,000 kc/s. Preliminary experiments in frequency multiplication were conducted using the principles of the harmonic amplifier, the multivibrator, and the synchronized oscillator.[2] The most effective multiplication was obtained with a self-excited oscillator operating in synchronism with a harmonic of an impressed frequency. A type '10 (7.5-watt) triode was employed in a tuned-grid oscillator circuit and the frequency from the standard was applied directly to the grid. A high value of grid-bias resistor was used and the regeneration was so adjusted that oscillations were just maintained. Correct operation was determined by a monitoring detector-amplifier loosely coupled to the oscillatory circuit. As the frequency of the latter was adjusted to approach the desired harmonic of the standard, the beat note between the two gradually decreased until, at a certain low value, it suddenly disappeared, showing that the harmonic of the standard-frequency source was now controlling the oscillator. Further adjustment of the tuning over a small range did not disturb this control. Adjustment beyond this range was indicated by the reappearance of the beat note in the telephones or loud speaker. The range of control or synchronization depended on the voltage and wave form of the input frequency, the type and relative power of the oscillator under control, and the order of multiplication.[3]

An examination of the operation of a synchronized oscillator was made with a cathode-ray oscillograph. One set of plates was connected to the control frequency source and the other to the oscillatory circuit. The latter was then tuned to various harmonics of the input frequency. Synchronization was indicated by a stationary figure.[4] At either end of the control range a Lissajous loop figure appeared with the number of loops corresponding to the harmonic number while at the center of the range these loops collapsed into a line or repeating figure. Interpretation shows that at the center of the control range the peaks of the fundamental and harmonic voltages are coincident in time regardless of polarity. A variation of tuning through the range produces a phase shift in the harmonic voltage wave of approximately plus or minus 90° or a total of 180°. This is independent of the order of harmonic at which the circuit is operating.

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[2] On some experiments in which two neighbouring maintained oscillatory circuits affect a resonating circuit. J. H. Vincent. Proc. Phys. Soc., London, vol. 22, p. 84, Feb. 15, 1920.
The automatic synchronization of triode oscillators. E. V. Appleton. Proc. Camb. Phil. Soc., vol. 21, p. 231, 1922.
Sur la synchronization harmonique des oscillations électriques. M. J. Mercier. Comptes Rendus, vol. 174, p. 448, Feb. 13, 1922.
De la synchronization harmonique et multiple. M. J. Mercier. Journal de Physique, vol. 5, p. 168, June 1924.
A new method of obtaining frequency stabilization of a transmitter by means of an oscillating quartz crystal. C. W. Goyder. E. W. & W. E., III, p. 717, December 1926.
Forced oscillations in a circuit with nonlinear resistance. B. van der Pol, Jr. Phil. Mag., vol. 3, p. 65, January 1927.
A new frequency transformer or frequency changer. I. Koga. Proc. I.R.E., vol. 15, p. 669, August 1927.
Über Erzwungene Schwingungen in Elektronenröhrenkreisen. H. Witte. Arch. f. Elektrot., vol. 23, p. 84, Nov. 5, 1929.
Le fréquencemètre étalon absolu du Laboratoire National de Radioélectricité. B. Decau. L'Onde Électrique, vol. 9, p. 449, October 1930.
Über die Mitnahmeerscheinungen an Röhrengeneratoren Bei Verschiedenen Frequenzverhaltnissen. H. Winter-Günther. Zeitschr. f. Hochf. Tech., vol. 37, p. 39, February 1931.
Synchronization of Westinghouse radio stations WBZ and WBZA. S. D. Gregory. Radio Engineering, vol. 11, p. 29, September 1931.

[3] See footnote 2, above.

[4] The cathode ray oscillograph. J. B. Johnson. Bell System Tech. Jour., vol. XI, p. 23, January 1932.

A succession of synchronized oscillators was required to attain the desired frequency for transmission. The first oscillator was tuned to the fundamental of the 100- or 200-kc/s standard to give an ouptut rich

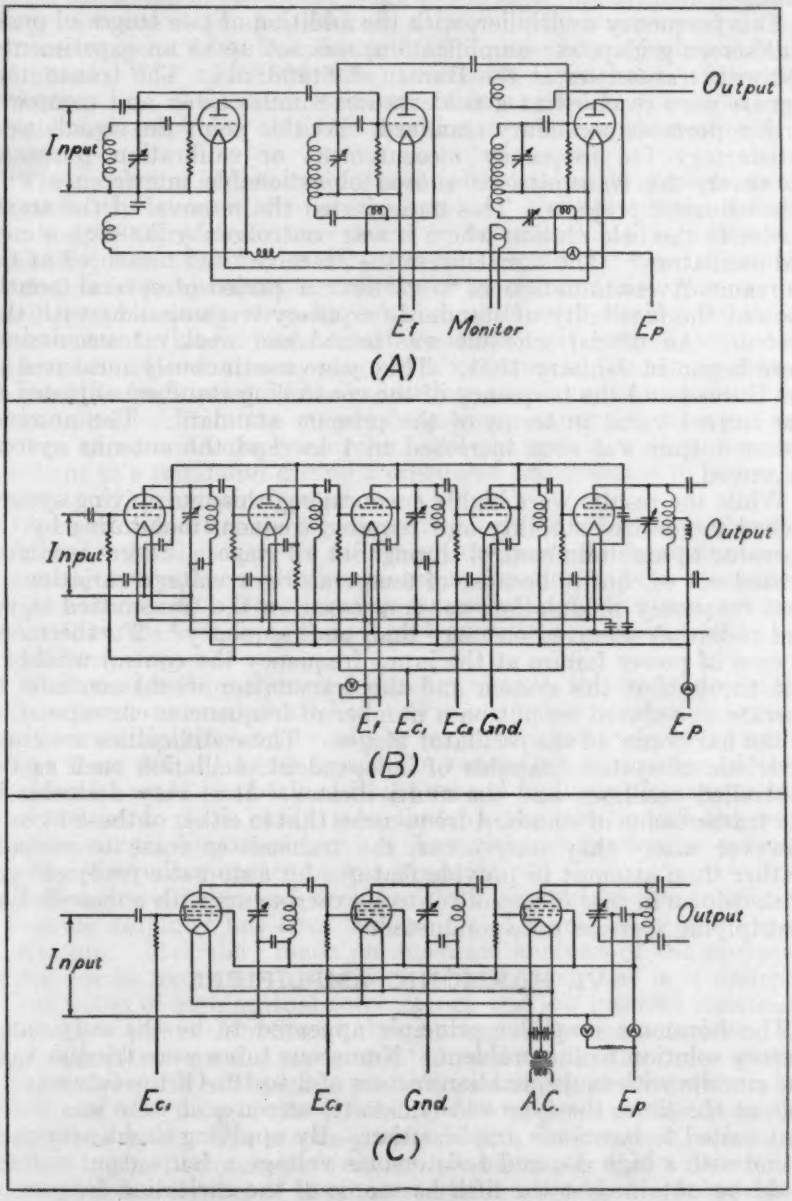

FIGURE 2.—*(A) Controlled-oscillator multiplier, (B) UX-865 harmonic amplifier, (C) Pentode harmonic amplifier.*

in harmonics. The second operated at 1,000 kc/s with a rich harmonic output, and, in turn, controlled a third oscillator at 5,000 kc/s; figure 2 (*A*). Type '10 tubes were used in each stage. Once they were set

in the middle of the control ranges, as indicated by the monitor, and allowed to reach constant temperature, the system would remain in a synchronized condition until disturbed by voltage or temperature changes.

This frequency multiplier, with the addition of two stages of push-pull screen-grid power amplification, was set up as an experimental 150-watt transmitter at the Bureau of Standards. The transmitted signals were received at a field station 8 miles away and compared with a portable secondary standard. At this point the signals were satisfactory for frequency measurement or calibration purposes. However, the transmissions caused objectionable interference with other Bureau projects. This necessitated the removal of the transmitter to the field station where it was controlled by 200-kc/s standard oscillators.[5] The signals were then received and measured at the Bureau. A continuation of tests over a period of several months showed the feasibility of standard-frequency transmissions with this system. An official schedule was issued and weekly transmissions were begun in January 1931. They were continuously measured at the Bureau and the frequency of the controlling standard adjusted to the correct value in terms of the primary standard. The nominal power output was soon increased to 1 kw and the antenna system improved.

While the results were highly encouraging, this multiplying system lacked the desired stability and required frequent monitoring by the operator to maintain control throughout all stages. If one oscillator drifted out of control because of temperature or voltage variations, a beat frequency modulation was impressed on the transmitted signal and radiation occurred on more than one frequency.[6] Furthermore, in case of power failure at the input frequency the control would be lost throughout the system and the transmitter would continue to operate at reduced output on a number of frequencies corresponding to the harmonics of the oscillator stages. These difficulties are characteristic of systems capable of independent oscillation such as the controlled oscillator and the multivibrator. It is very desirable in the transmission of standard frequencies that in either of these events, however rarely they may occur, the transmitter cease to radiate. Rather than attempt to provide features for automatic readjustment or shutdown in case of loss of control, experiments with nonoscillating multiplying systems were conducted.

VI. HARMONIC AMPLIFIERS

The harmonic amplifier principle appeared to be the only satisfactory solution to the problem. Numerous tubes were tried in various circuits with multiplication factors of 2 to 10. Of the tubes available at the time, the type 865 (7.5-watt) screen-grid tube was found best suited to harmonic amplification. By applying slight over-excitation with a high d-c and resistor-bias voltage a fair output voltage could be obtained at the fifth harmonic of the excitation frequency. The low current consumption and plate dissipation of this tube resulted in economical operation. It was necessary, however, to supply additional amplification between two such multiplying stages. An imped-

[5] A 200-kilocycle piezo oscillator. E. G. Lapham. B. S. Jour. Research, vol. 11, p. 50, July 1933.
[6] Stabilisateurs piezo-électriques II. J. Jammet. L'Onde Électrique, vol. 7, p. 63, February 1928.

ance-coupled, rather than tuned, amplifier was employed. This gave ample grid swing on the succeeding tube, simplified adjustments, and added stability. Accordingly, a complete multiplier unit was built, consisting of one tuned stage at 200 kc/s, an impedance-coupled stage, a tuned stage at 1,000 kc/s, a second impedance-coupled stage, a tuned stage at 5,000 kc/s, figure 2 (*B*), followed by a push-pull buffer amplifier. The type 865 tube was used throughout. Interstage shielding was not used in the experimental model, but an external shield was employed to avoid reaction from the power amplifying stages.

The operation of this type of multiplier was in all respects similar to that of the usual frequency doubler. Neither supply voltages nor tuning adjustments were found to be critical. A high degree of stability was obtained which was unaffected by any reasonable variation in temperature or voltage or mechanical disturbance. An oscillographic study revealed a phase shift with tuning, similar to that noted in the synchronized oscillator. If such a shift were induced in a low-frequency stage by a variation of the tuning control, it would be multiplied by the succeeding stages and would result in a larger phase shift in the output frequency, amounting to a net gain or loss of several complete cycles. All changes in tuning, however, are kept to a minimum during a scheduled transmission to insure the stability of the output frequency.

The main object of the experiments, as stated before, was therefore achieved. In the event of failure of any part of the equipment or input frequency, the multiplier ceased to function and the transmitter could not radiate. There was no source of radio-frequency voltage other than the standard, the entire transmitter operating only as an amplifier.

While designed for a single-frequency output, this frequency multiplier offered unusual flexibility. With a 200-kc/s input frequency the first multiplying stage could be set at any harmonic in its tuning range from 600 to 1,800 kc/s. Corresponding harmonics of these frequencies could be obtained in the second multiplying stage as high as 8,000 kc/s. It is easily seen that by the addition of the usual doubling or tripling amplifiers a wide variety of frequencies covering the high-frequency spectrum was available.

The choice of tubes and circuit operating conditions for an efficient harmonic amplifier has been the subject of much study and experimentation. Marique [7] made an algebraic analysis of the operation of triodes as frequency multipliers. He showed that it is desirable to use tubes of high mutual conductance and low internal resistance. Of the low-power American tubes having these characteristics, the best examples were the types '50, '45, and '10, in the order named. This analysis did not assume positive grid swing or saturation plate current of the tube, both of which were present in the frequency multipliers used. The screen-grid type 865, for instance, was found to have marked advantages over any of the triodes above mentioned, although it had neither of the characteristics advocated. It is evident that a high amplification factor is also advantageous. The advantages of this tube lay in the greater amplitude of harmonics, smaller amplitude of fundamental component due to low interelectrode capacity, and less critical bias voltage required.

[7] Note sur le Calcul des Étages Multiplicateurs de Fréquence à Triodes. J. Marique. L'Onde Électrique, vol. 8, p. 1, January 1929.

The most promising tube for this purpose was the pentode type which had in addition to a screen grid, a suppressor grid for the elimination of secondary emission from the plate. This tube, had all the desirable characteristics mentioned above, namely, a high mutual conductance and amplification factor and a relatively low internal resistance. A harmonic amplifier was built at the Bureau of Standards using the type 247 pentode with unusually good results; figure 2 (*C*). A multiplication of 5 to 1 was obtained in one tube with a slight voltage gain. No intermediate amplification was required. Three tubes were sufficient to give a peak output of more than 100 volts at 5,000 kc/s from an input of less than 5 volts at 200 kc/s. This unit was installed and given thorough tests in an auxiliary transmitter before incorporation in the 1-kw transmitter used in the scheduled transmissions. These tests showed the type 247 multiplier to be fully as stable and to have a lower noise level than the type 865 multiplier, while the tube and operating costs were much reduced. As in the previous multiplier units, a type 865 push-pull buffer amplifier was used.

In the experimental 1-kw transmitter, the multiplier unit with buffer amplifier was followed by two stages of push-pull intermediate type 860 (150-watt) amplification and a push-pull type 861 (1-kw) power amplifier. The latter was coupled through a transmission line to a horizontal half-wave antenna approximately one eighth wave length above ground. An antenna of greater height was not permissible because of the proximity of an experimental flying field. The equipment was in weekly operation from March 1931 to November 1932, at which time a new transmitting station was completed at Beltsville, Md., about 13 miles from the main Bureau laboratory. The experimental transmitter was then moved to the new location, a new rectifier-type power supply provided, and higher antennas constructed. This transmitter, together with the high-voltage rectifier and control-frequency standard, are shown in figure 3.

VII. 30-KW TRANSMITTER

A great step in the progress of the standard-frequency service was marked by the purchase and installation, late in 1932, of a high-power transmitter of the most advanced design. It has a continuous frequency range of 4,000 to 26,000 kc/s and a nominal power output of 30 kw at the lower frequencies. It consists of a 1-kw exciter unit, with its associated rectifier power supply, a 30-kw power amplifier, main-plate rectifier, plate transformer, tap-changing contactors, and a water-cooling system for the large transmitting tubes. A block diagram of the equipment is given in figure 4, while a simplified schematic diagram is shown in figure 7. Photographs of the major units of the installation at the Beltsville field station are shown in figures 5 and 6.

The exciter unit, together with its rectifier, is a complete and independent 1-kw transmitter. It contains a 7.5-w type 865 oscillator or buffer amplifier, *B*, figure 4, four intermediate type 860 screen-grid, fundamental, doubling, or tripling amplifiers (*C*), (*D*), (*E*), (*F*), and a power amplifier using two type 861 (500-w) screen-grid tubes in parallel (*G*). A frequency multiplier, as shown in figure 2 (*C*) and at *A* in figure 4, is built as an integral part of the unit. With a

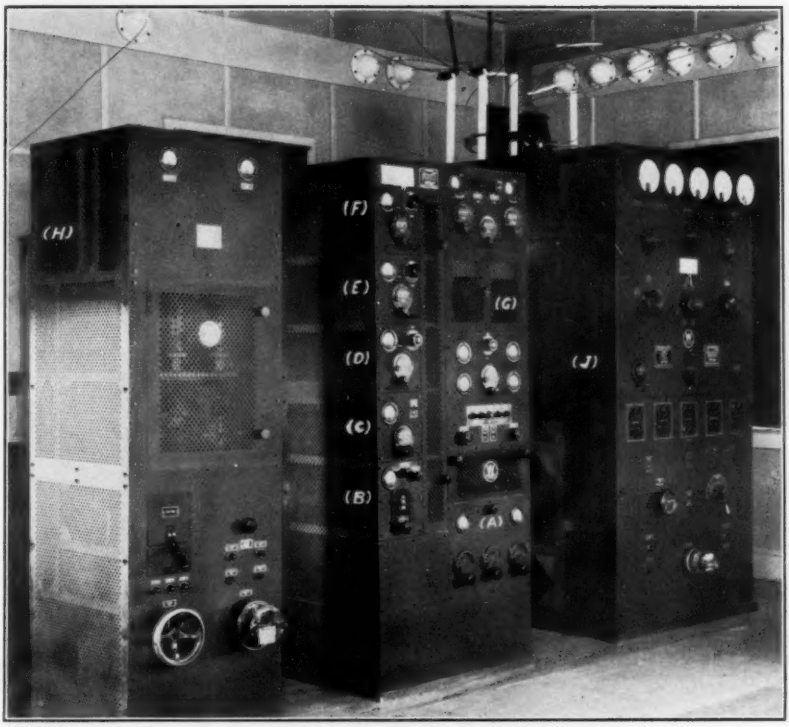

FIGURE 5.—*30-kw transmitter units on main floor of Beltsville, Md., station.*

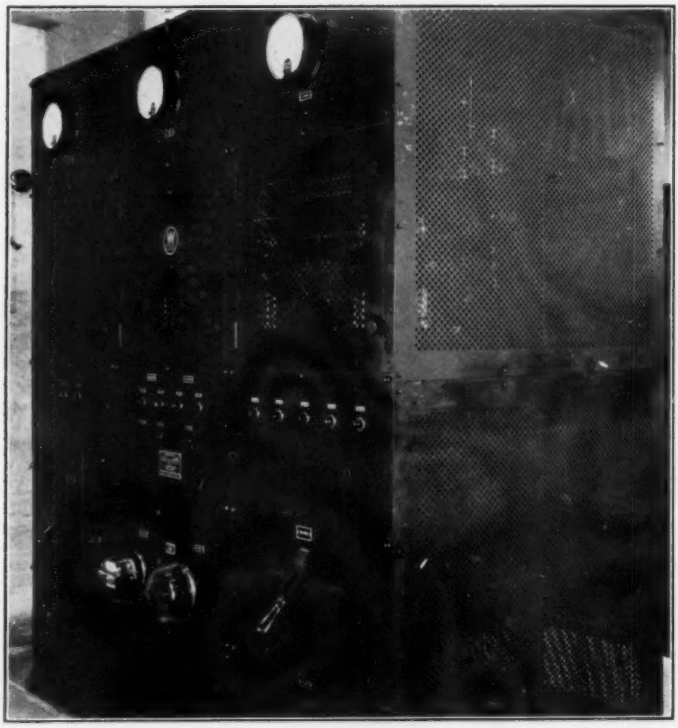

FIGURE 6.—*30-kw transmitter units in basement of Beltsville, Md., station.*

200-kc/s input from a standard, this transmitter will deliver from 600 to 1,200 watts to any type of antenna or to the power amplifier grids at 5,000 kc/s or any harmonic up to 20,000 kc/s. With the type 865 (7.5-w) tube used as a self-excited oscillator, the unit will operate in a similar manner on any frequency from 4,000 to 26,000 kc/s.

The power-amplifier unit, figure 4 (*J*), employs two type 858 (20-kw) water-cooled tubes in a push-pull, tuned-grid, tuned-plate circuit arrangement. Coupling to the antenna is effected through 600-ohm matched-impedance transmission lines. The frequency is continuously variable from 4,000 to 26,000 kc/s by controls on the front panel of the unit. The plate inductors and associated switches

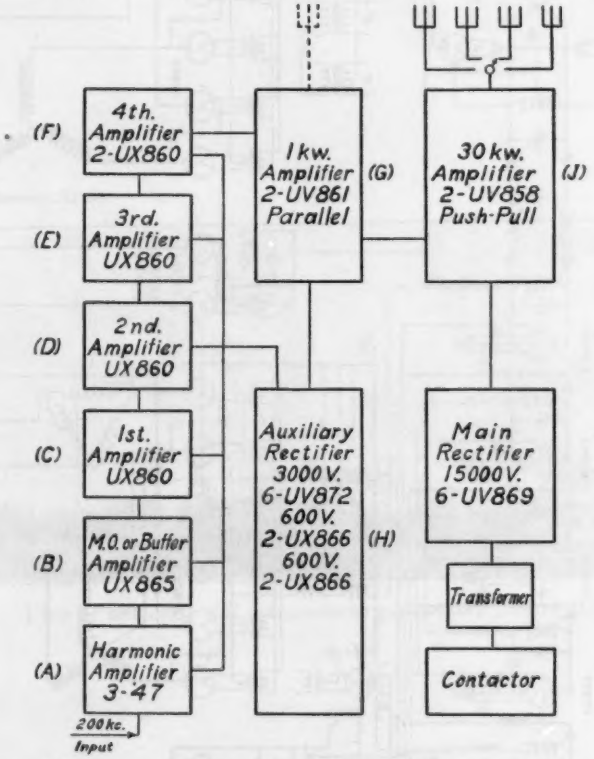

FIGURE 4.—*Block diagram of 30-kilowatt transmitter*

as well as the plates of the tubes are cooled by circulating distilled water. Complete control of all starting operations, plate voltages, and frequency adjustment is obtained through switches and dials on the power amplifier and exciter front panels. This affords great flexibility and convenience in operation.

All plate and bias voltages are obtained from rectifiers using hot-cathode mercury-vapor tubes. The power-amplifier plate voltage of 7,000 to 15,000 volts is supplied by the main rectifier equipment, using six type 869 tubes in a full-wave three-phase circuit. The exciter plate voltages of 1,500 and 3,000 volts and the power-amplifier bias voltage are supplied from rectifiers using type 872 tubes, while lower-plate and bias voltages are supplied from type 866 tubes. The

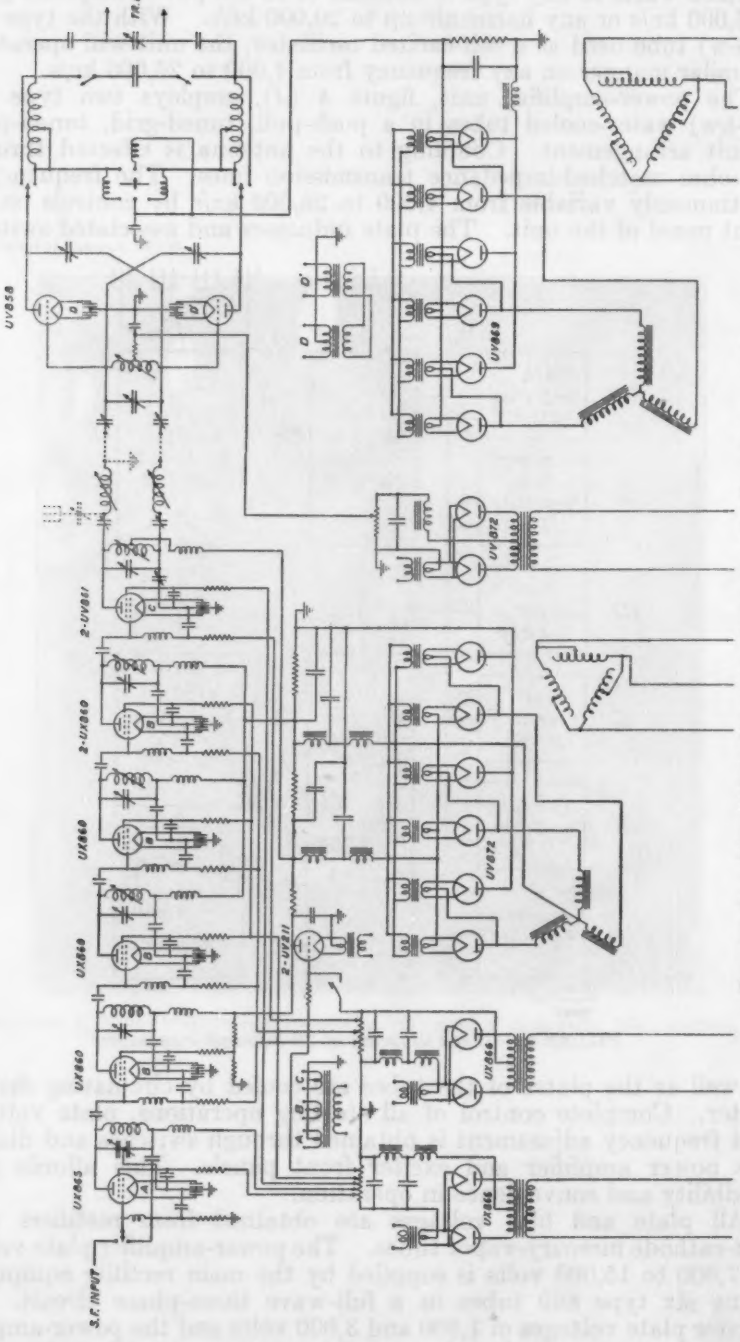

FIGURE 7.—*Simplified schematic diagram—80-kilowatt transmitter.*

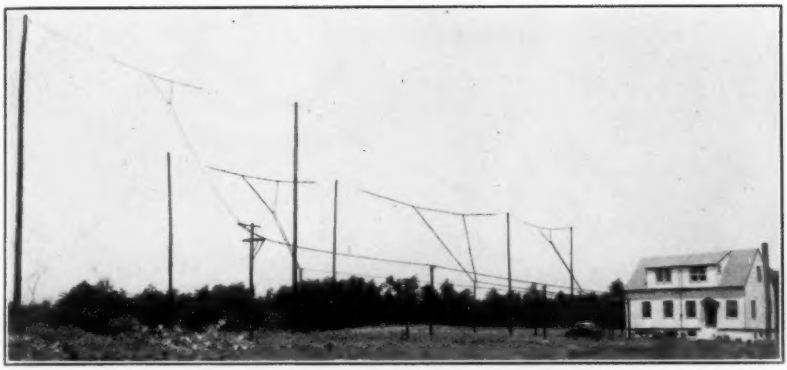

FIGURE 8.—*View of antennas and transmitting station building at Beltsville, Md.*

UNIV. OF MICH.

main plate voltage is adjustable by means of large contactors which change the taps on the primary of the high-voltage three-phase transformer. A similar, but less elaborate system, is used to regulate the exciter plate voltages.

The water-cooling system for the power amplifier consists of two large radiators with associated fans, a centrifugal water pump, and a storage tank for distilled water. All connections between units are of brass pipe to reduce corrosion and resulting increase in the water conductivity.

An elaborate interlocking system is provided between all units to effect immediate shut-down of the transmitter in case of excess plate current, low filament voltages, excess water temperature, low water pressure or flow, or the opening of any access door in the equipment. This insures protection to tubes and personnel in case of improper operation or inadvertent entrance to any compartment for inspection or adjustment while operating voltages are on.

The limitation of the transmitted frequencies to 5,000 kc/s and harmonics thereof made the use of fixed-frequency antennas advantageous, especially in view of the use of matched-impedance transmission lines to the power amplifier. A single-wire horizontal half-wave doublet was therefore installed for each operating frequency, 5,000, 10,000, 15,000, and 20,000 kc/s. The antennas were suspended from wood poles 65 ft in height. This gave each antenna a height much more than a quarter wave length above ground and a substantial amount of low-angle radiation. They were oriented in a north-south direction so that the slight directional characteristics favored the western part of the United States. A view of the station building and antenna system is shown in figure 8.

VIII. RESULTS

Since the inauguration of the 5,000-kc/s transmissions in January 1931, there has been a progressive increase in accuracy of the transmitted frequency. In order to maintain the frequency continuously in agreement with the national primary frequency standard, the signals are received and the frequency continuously recorded at the main laboratory of the Bureau of Standards, 13 miles distant. Adjustments of the control standard in the transmitting station to agreement with the national primary standard are made just prior to each scheduled transmission. The constancy of this control standard is such that this agreement is usually maintained over a 2-hr schedule without any readjustment being required. The average deviations of the transmitted frequency from the national standard are about two parts in a hundred million, while extreme variations may reach five parts in a hundred million.

Because of phenomena which may occur in the transmitting medium the frequency as received at some distant points may sometimes not have this accuracy.[8] Apparent frequency changes greater than a part in 10 million are sometimes noted at a distance of 13 miles when there is ample evidence that they are not present in the transmitted wave.

[8] Radio dissemination of the national standard of frequency. J. H. Dellinger and E. L. Hall. Radio Engineering, vol. 12, p. 23, May 1932.

The 30-kw transmitter has been used regularly for the standard frequency schedule since April 1933. The increase in power has resulted in marked improvement in the dependability of the signals, especially in those areas where reception is ordinarily difficult. Reports of reception have come from every section of the United States as well as points in Alaska, the Canal Zone, England, and Italy. In localities where receiving conditions are at all favorable observers report successful use of the signals for frequency comparison purposes.

WASHINGTON, August 26, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP631

Part of Bureau of Standards Journal of Research, vol. 12, January 1934

DATA ON THE SPECTRAL ERYTHEMIC REACTION OF THE UNTANNED HUMAN SKIN TO ULTRAVIOLET RADIATION

By W. W. Coblentz and R. Stair

ABSTRACT

This paper gives a revision and an extension in spectral range of the data, previously published [1] on the spectral erythemic reaction of the untanned skin.

The erythemic reaction is a convenient and accurate indicator of the tolerance of the human skin to ultraviolet radiation. Hence, before irradiating large areas, a preliminary exposure should be made on a small area to determine the time to produce a minimum perceptible erythema, thus avoiding burns.

A knowledge of the spectral erythemic response is, therefore, of importance in evaluating the ultraviolet output of a lamp. By means of data on the spectral erythemic reaction on the skin and a simple physical measurement [2] of the radiant flux emitted by the lamp, it is possible to calculate the approximate time of exposure that may be made without causing severe burns on the average pigmented skin.

In a previous communication [3] data were given on the spectral erythemic response of the untanned human skin to ultraviolet radiation, in the wave length range extending from 2482 to 3130 A.

In the meantime Rüttenauer [4] presented data on the erythemic response to filtered radiation of wave length 3261 A, which he obtained from a low-pressure cadmium arc lamp. He found that the spectral erythemic response at 3261 A is 0.003 to 0.004 that of the emission line at 2967 A; and that this erythema has the property of changing rapidly into pigmentation. The color of the erythema and of the pigmentation is similar to that produced by sunlight.

Experiments seem to indicate that, in the spectral range where these two reactions are produced, the longer the wave length the greater appears to be the pigmentation [5] relative to the erythemic reaction. Furthermore, since, for the long wave lengths, pigmentation begins before the erythema has disappeared (also there is a

[1] Coblentz, Stair, and Hogue, B.S.Jour. Research, vol. 8 (RP433), p. 541, 1932.

[2] Tests of a Balanced Thermopile and Filter Radiometer as a Standard Ultraviolet Dosage Intensity Meter, W. W. Coblentz, R. Stair, and J. M. Hogue, B.S.Jour. Research, vol. 8 (RP450), p. 759, 1932. Also see Acceptance of Sun Lamps, by the Council on Physical Therapy, Jour. Am. Med. Association, vol. 100, p. 1863, June 10, 1933.

[3] See footnote 1.

[4] Rüttenauer, Proc. IIe Congrès International de la Lumière, Copenhagen, p. 72, Aug. 18, 1932, published by Engelsen and Schroeder, Copenhagen.

[5] Uhlmann, Strahlentherapie, 35, p. 361, 1930; also papers by Gutman (cited by Uhlmann), and by Hausser and Vahle, etc., cited in our previous publication, reference 1.

similarity in color of the skin for these two reactions) there is difficulty in deciding when the erythema has completely disappeared.

Because of the rapid formation of pigment (tanning) after exposure to the emission line at 3130 A, the writers experienced difficulty in deciding when the erythema had completely disappeared. As a consequence, there was a possibility of overestimating the magnitude of the erythemal reaction.

It is possible that Rüttenauer may have experienced a similar difficulty. Nevertheless, in spite of the smallness of the erythemal reaction measured, Rüttenauer's data are useful in establishing the long wage-length limit of spectral erythemic reaction. Accepting his values, as given, the writers have extended their curve of spectral erythemic reaction to wave lengths longer than 3150 A, previously published. Furthermore, to meet the needs for higher accuracy, they have made a further study of, and have revised, the previously published data, all of which are given in table 1. The new data in the spectral range of 3150 to 3300 A have but little effect upon the evaluation of the erythemogenic efficiency of therapeutic lamps, given in previous papers.

TABLE 1

The relative spectral erythemic response of the untanned human skin, of average pigmentation, to equal amounts of radiant energy, based upon the measurements of Hausser and Vahle (spectrally homogeneous radiation, 1922 and 1927); of Luckiesh, Holladay and Taylor (filter method, 1930); of Coblentz, Stair, and Hogue, using (in 1931) spectrally homogeneous radiation, and (in 1932) heterogeneous radiation from a "cold quartz" mercury vapor lamp, having 98 percent of the erythemogenic radiation in the emission line at 2537 A; and of Rüttenauer (IIe Internat. Congrès de la Lumière, Copenhagen, 1932) using the filtered cadmium line at 3261 A. The asterisk (*) indicates emission lines of the mercury arc.

Wave length (angstroms)	Erythemic response	Wave length (angstroms)	Erythemic response
2,400	0.56	2,894*	0.25
2,446*	.57	2,900	.31
2,482*	.57	2,925*	.70
2,500	.57	2,950	.98
2,537*	.55	2,967*	1.00
2,576*	.49	3,000	.83
2,600	.42	3,022*	.55
2,654*	.25	3,050	.33
2,675*	.20	3,100	.11
2,700*	.14	3,130*	.03
2,753*	.07	3,150	.01
2,804*	.06	3,200	.005
2,850	.09	3,250	.003
2,857*	.10	3,300	.000

WASHINGTON, September 30, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP632

Part of Bureau of Standards Journal of Research, vol. 12, January 1934

STUDIES OF THE IONOSPHERE AND THEIR APPLICATION TO RADIO TRANSMISSION [1]

By S. S. Kirby, L. V. Berkner, and D. M. Stuart

ABSTRACT

Observations of the virtual height of the ionosphere and its variations carried out at the Bureau of Standards during the period of September 1930 to April 1933 are reported and discussed. The pulse method of Breit and Tuve was used with a visual recording technique developed by the Bureau of Standards.

In general, a number of layers were discernible, the major daytime layers being the lower or E layer at about 100 to 120 km virtual height, an F_1 layer at about 180 km virtual height, and an F_2 layer at about 240 km virtual height. The relative electron densities of these layers were determined by measuring the critical penetration frequencies where possible. The E and F_1 layer critical frequencies were highest at summer noon and fell off both diurnally and seasonally as the angle of the sun's rays with the vertical increased. Abnormally strong E layer ionization occurred occasionally at irregular intervals. The F_1 layer showed magneto-ionic splitting during the day. There was some correlation between F_1 layer ionization and magnetic storms.

The F_2 critical frequency was greatest on a summer evening, and greater on a winter noon than on a summer noon. From this evidence it is believed that the F_2 critical frequency may be determined by some other factor than penetration, such as absorption.

Scattered reflections of long retardation were observed on frequencies considerably higher than the F_2 critical frequency.

CONTENTS

		Page
I.	Historical summary	15
II.	Experimental method	19
III.	Investigations of the E layer	23
IV.	Investigations of the F_1 layer	28
V.	Investigations of the F_2 layer	38
VI.	Scattered reflections	47
VII.	Some correlations with results of radio transmission	48

I. HISTORICAL SUMMARY

Marconi's first successful trans-Atlantic radio transmission in 1901 aroused a great deal of discussion regarding the propagation of radio waves around the curvature of the earth's surface. Theoretical reasoning showed that the phenomena could not be due to diffraction alone. In 1902 A. E. Kennelly [2] published the first suggestion of an ionized upper region in the atmosphere in connection with radio wave propagation. He showed that this region, for the lower limit of which he calculated provisionally a height of 80 km, would be conducting. It is interesting to note that Kennelly used the expression "electrically

[1] Read at URSI meeting at Washington, Apr. 27, 1933, and at the Annual Convention of the I.R.E. at Chicago, June 26, 1933.

[2] A. E. Kennelly, Electrical World & Engineer, vol. 39, p. 473, Mar. 15, 1902.

conducting strata" indicating that he had in mind several layers. If we may quote one sentence from Kennelly's 1902 paper his ideas on this subject will be indicated clearly. He wrote: "It seems reasonable to infer that electromagnetic disturbances emitted from a wireless sending antenna spread horizontally outwards, and also upwards, until the conducting strata of the atmosphere are encountered, after which the waves will move horizontally outwards in a 50-mile layer between the electrically-reflecting surface of the ocean beneath, and an electrically-reflecting surface, or successive series of surfaces, in the rarified air above." A few months later Oliver Heaviside[3] independently set forth the idea that a conducting layer in the upper atmosphere might guide radio waves.

The theory of propagation of light waves through a system of molecules was given by H. A. Lorentz[4] in 1909. This theory was applied to radio wave propagation in the ionosphere by Eccles[5] and Larmor.[6] Eccles assumed an upper layer so intensely ionized as to reflect the waves without penetration and an ionization of the middle atmosphere which bent the waves. He considered only the motions of the heavy ions. He showed that the action of free ions was to increase the phase velocity of the waves in the medium so that the index of refraction was decreased to a value less than unity. Thus the waves were bent by refraction rather than reflection. Larmor emphasized the importance of considering free electrons of such a long free path that absorption was negligible and sketched a theory of refraction based upon these ideas. Being lighter than the ions, comparatively few electrons were necessary to produce sufficient bending of the rays. The foundations for a theoretical discussion of the action of the ionosphere on radio wave propagation are to be found in these two papers.

In his 1912 paper and again in 1924, Eccles[7] stated that two layers, one a high permanently ionized layer, and the other a lower layer ionized daily by sunlight, were required to explain the phenomena then observed.

Appleton and Barnett,[8] in 1925, reported direct evidence of the existence of a reflecting layer. They employed both the frequency change method and the angle of incidence method using a frequency of about 750 kc/s. They estimated the virtual height to be about 80 km. A few months later Breit and Tuve[9] independently reported similar evidence using the pulse or group retardation method developed by them, and employing a frequency of about 4,200 kc/s. At this time they reported virtual heights of 80 km and 160 km. A comprehensive paper was published by each of these groups of workers a few months later.[10] [11] In the latter paper Breit and Tuve reported virtual heights from about 90 km to 225 km. In the light of later developments, it is evident that they were getting reflections from both E and F regions. Breit and Tuve at this time also used other frequencies such as 7,500 kc/s, at which they sometimes received reflections but not always. They observed that reflections varied rapidly both in amplitude and position.

[3] Oliver Heaviside, Encyclopedia Britannica, Tenth Edition, vol. 33, p. 215, Dec. 19, 1902.
[4] Lorentz, Theory of electrons, Leipsig, 1909.
[5] Eccles, Proc.Roy.Soc., 87A, p. 79, 1912.
[6] Larmor, Phil.Mag., vol. 48, p. 1025, 1924.
[7] Eccles, Proc.Phys.Soc., vol. 37, pp. 3D and 43D, November 1924
[8] Appleton & Barnett, Nature, vol. 115, Mar. 7, 1925.
[9] Breit and Tuve, Nature, vol. 116, p. 357, Sept. 5, 1925.
[10] Appleton and Barnett, Proc.Roy.Soc.A, vol. 109, p. 621, December 1925
[11] Breit and Tuve, Phys.Rev., vol. 28, p. 554, September 1926.

At about the same time, studies of the ionosphere were being made by Taylor and Hulburt[12] using the skip distance method. They calculated daytime virtual heights of from 155 to 240 km.

In 1927 Appleton[13] working at 750 kc/s detected a sudden change in the virtual height of the layer during some early morning measurements, and concluded that there were 2 layers at night, one at a virtual height of about 100 km and the other at a virtual height of about 240 km.

In 1928 Breit, Tuve, and Dahl[14] reported daytime virtual heights from about 100 km to 225 km with multiples of the 225 km values.

In 1929 and 1930 Appleton and Green,[15][16] working at about 3,000 kc/s reported evidence of sudden jumps of the virtual height of the layer in the daytime and concluded that the two layers, *E* and *F*, existed both day and night. They also pointed out that this interpretation fitted in with the earlier results of Breit, Tuve, and Dahl.

In 1931 Schafer and Goodall,[17] working at 1,604 kc/s and 3,088 kc/s simultaneously, found abrupt increases in virtual height during the late afternoon and corresponding decreases in the early morning. However, the afternoon increase in virtual height occurred about 2 hours earlier for 3,088 kc/s than for 1,604 kc/s and in the morning the virtual height for 1,604 kc/s decreased before that for 3,088 kc/s. These results were interpreted as evidence of two layers.

In 1931 Gilliland, Kenrick, and Norton[18] varied the frequency from 1,600 to 8,650 kc/s and found evidence that the 2 layers existed simultaneously during the day for frequencies between 3,000 and 5,000 kc/s. They also discussed the effect of the *E* layer on the retardation of pulses going to the *F* layer and showed that for the critical-penetration frequency long retardations should be expected.

Evidence that there are two or more layers has been found in practically all subsequent work of this type regardless of the method used. The frequency change method and the angle of incidence method were developed in England, and the pulse method by Breit and Tuve in the United States. The British school has used the frequency change method for normal incidence experiments almost exclusively until the last three years. Since then, it has taken up the pulse method of Breit and Tuve, probably because the complex phenomena observed at the higher frequencies could not be interpreted by the frequency change method. The American school has used the pulse method of Breit and Tuve exclusively for vertical incidence experiments from the beginning of this work in 1925 and has developed a technique for rapid and continuous measurements which facilitates detailed studies of layer changes. The German[19][20] school also has used the pulse method of Breit and Tuve.

Hafstad and Tuve [21] extended the pulse method to measure the rate of change of the virtual height of a layer by the determination of the rate of change of radio-frequency phase of separate downcoming echoes.

[12] Taylor and Hulburt, Phys.Rev., vol. 27, p. 189, February 1926.
[13] Appleton, Nature, p. 330, Sept. 3, 1927.
[14] Breit, Tuve, and Dahl, Proc.I.R.E., vol. 16, p. 1236, September 1928.
[15] Appleton and Green, Nature, vol. 123, p. 445, Mar. 23, 1929.
[16] Appleton and Green, Proc.Roy.Soc. A., vol. 128, p. 159, July 1930.
[17] Schafer and Goodall, Proc.I.R.E., vol. 19, p. 1434, 1931.
[18] Gilliland, Kenrick and Norton, B.S. Jour. Research, vol. 7, p. 1083, 1931. Proc.I.R.E., vol. 20, p. 286, 1932.
[19] Goubau and Zenneck, Zeitschrift für hochfrequenztechnik, vol. 37, p. 207, 1931.
[20] Rukop and Wolf, Zeitschrift für technische physik, vol. 3, p. 132, 1932.
[21] Hafstad and Tuve, Proc.I.R.E., vol. 17, p. 1786, 1929.

T. L. Eckersley [22] has developed and used a valuable method for long-distance studies of the ionosphere by means of facsimile transmissions.

In 1925 Appleton [23] and Nichols and Schelleng,[24] independently, pointed out that radio-wave refraction and absorption in the ionosphere should be considerably modified by the earth's magnetic field. Nichols and Schelleng showed that, in the simple cases in which a radio wave is propagated parallel or perpendicular to the earth's magnetic field, it would be split into 2 components by magnetic double refraction and, in general, one of these components would be more highly absorbed than the other. They also showed that there should be a critical absorption frequency at about 1,400 kc/s.

In 1927 Breit [25] showed quantitatively the effect of the earth's magnetic field on a ray propagated in any direction with respect to the terrestrial magnetic field. A few months later Appleton [26 27 28] independently solved the same problem and gave an equation for the index of refraction which we shall use later on.

In 1928 Appleton and Ratcliffe [29] found that downcoming waves of 750 kc/s in England were circularly polarized with a left-handed rotation due to the absorption of the other component and predicted that under similar circumstances in the southern hemisphere the waves would be circularly polarized with a right-handed rotation. In 1932 Green,[30] working in Australia, reported experiments verifying this prediction.

In this brief historical review an attempt has been made to sketch the order of development of some of the principal phases of studies of the ionosphere. No attempt has been made to write a comprehensive review covering all the literature to date. Much of the more recent literature will be referred to during the discussion of our own work later on in this paper.

With regard to the nomenclature, the authors have adopted the general term "ionosphere" suggested by Dr. Watson Watt, to designate all the ionized region of the earth's atmosphere. We have previously called this region the Kennelly-Heaviside layer in honor of the men who contributed the original suggestions for this method of radio-wave propagation.

Although several layers are spoken of as if they existed separately with nonionized regions between them, it is not believed that such is the case, but rather that there exists one ionized region whose ionization varies with the height in such a manner that the retardations of radio waves fall into fairly definite groups. These retardations which determine the virtual height are due, first, to the actual height of the reflecting layer and, second, to the reduction in group velocity of the pulse caused by passing through lower ionized regions. The resultant virtual heights fall into fairly definite groups, but the real heights of the layers and the ionization between them is not known. The ionization between layers need not be less than that of the lower layer.

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[22] T. L. Eckersley, J.I.E.E., vol. 71, p. 405, 1932.
[23] Appleton, Proc. Phys. Soc., vol. 37, p. 22 D, Feb. 15, 1925.
[24] Nichols and Schelleng, Bell System Tech. Jour., vol. 4, p. 215, April 1925.
[25] Breit, Proc.I.R.E., vol. 15, p. 709, August 1927.
[26] Appleton, Proc.U.R.S.I., p. 2, October 1927.
[27] Appleton, J.I.E.E., vol. 71, p. 642, 1932.
[28] Appleton and Naismith, Proc.Roy.Soc. A, vol. 137, 1932.
[29] Appleton and Ratcliffe, Proc.Roy.Soc.A, vol. 117, p. 576, 1928.
[30] Green, Radio Research Board Report no. 2, Melbourne.

II. EXPERIMENTAL METHOD

The observations reported in this paper were carried out during the period of September 1930 to April 1933, as one part of a program to obtain more complete information than has been heretofore available about the ionosphere and its variations, and their relation to radio transmission.

The method used was the "pulse" or group retardation method of Breit and Tuve.[31] This consists of the transmission of a short pulse of about 2×10^{-4} seconds' duration. Part of this pulse travels along the ground to the receiving set and is called the "ground" or reference pulse. Part of the pulse also travels from the ground to any reflecting or refracting medium and back to the ground one or more times. From the measurable difference in time between the arrival of the ground wave and the reflected waves, a virtual height can be computed for the source of each reflection. The virtual height in kilometers as determined by these time differences is indicated directly by means of suitable apparatus at the receiving station.

It has been shown that the existence of free ions in space causes a reduction in the refractive index[32 33 34] which, when sufficient, results in the complete bending of an electromagnetic wave back to the earth. When the angle of incidence is nearly normal, and the frequency is known, the refractive index can be computed, and the ion content at the virtual height indicated can be estimated. In this discussion this reduction in refractive index is stated in all cases in terms of an equivalent electron density. The effect of a heavy ion will be proportional to the square of its charge and inversely proportional to its mass. A plane wave solution of Maxwell's equations shows that, for a wave propagated in a medium of dielectric constant ϵ and conductivity σ, the index of refraction is given by

$$n=\sqrt{\frac{\epsilon}{2}+\sqrt{\frac{\epsilon^2}{4}+\left(\frac{2\pi c^2\sigma}{\omega}\right)^2}} \tag{1}$$

where c = velocity of light
$\omega = 2\pi$ times the frequency.

It is shown by Epstein[35] that unless the conductivity σ is negligible, total refraction cannot occur. When σ is neglected, the refractive index becomes

$$n=\sqrt{\epsilon}=\sqrt{1-\Delta\epsilon} \tag{2}$$

where $\Delta\epsilon$ = reduction in dielectric constant due to free electrons. From Snell's law $n \sin \phi_r = \sin \phi$ where ϕ_r = angle of refraction and ϕ = angle of incidence. Then at the apex of the ray path $\sin \phi_r = 1$ and $n = \sin \phi = \sqrt{1-\Delta\epsilon}$

From the work of Lorentz it has been shown that the index of refraction of a frictionless electron gas is given by

$$n^2=1-\frac{4\pi Ne^2}{\omega^2 m+a(4\pi Ne^2)} \tag{3}$$

[31] See footnotes 8 and 10, p. 16. Also Breit and Tuve, Terr. Magnetism, vol. 30, p. 15, March 1925.
[32] See footnotes 3, 4, and 5, p. —.
[33] Baker and Rice, Jour. A.I.E.E., vol. 45, p. 535, 1926.
[34] Pedersen, Propagation of radio waves, Ch. 6, Copenhagen, 1927.
[35] P. S. Epstein, Proc. National Academy of Science, 1930, pp. 37 and 627.

where

N = number of electrons per cm^3
ω = angular frequency
e = electronic charge in esu.

The value of the constant "a" has been the subject of considerable discussion in recent literature. Lorentz put and stated that

$$a=\frac{1}{3}+S$$

the value of the constant S would in general be difficult to determine. He has, however, shown that $S=0$ for a medium, the scattering elements of which have a regular cubical arrangement.

The earlier writers [36] on the theory of the Kennelly-Heaviside layer put $a=0$ in their equations. This resulted in a value of

$$\Delta\epsilon=\frac{4\pi Ne^2}{\omega^2 m} \tag{3a}$$

More recently, however, Appleton [37] has called attention to the fact that "a" probably has a value different from zero. Hartree [38] has advanced reasons for believing that, in a medium such as the ionosphere, the value of "a" is very nearly equal to ⅓.

Because of the uncertainty concerning the value of "a", we have used both the value of 0 and ⅓ for numerical calculations.

From equation (3)

$$n=\sin\phi=\sqrt{1-\frac{4\pi Ne^2}{\omega^2 m+a(4\pi Ne^2)}} \tag{4}$$

When ϕ is made small by locating the transmitter and receiver near together, $\sin^2\phi=0$ very nearly, and selecting f_c as the lowest frequency at which the wave passes through the layer (the critical frequency) we have

$$\text{putting } a=\frac{1}{3} \text{ in (3)} \qquad N=1.86\times10^{-8}f_c^2 \tag{5}$$

$$\text{or, putting } a=0 \text{ in (3)} \qquad N=1.24\times10^{-8}f_c^2 \tag{5a}$$

The value of N is taken as a measure of the maximum ionization of the layer.

It has been shown [39] that the refractive index is modified by the earth's magnetic field. In general, two refractive indices are possible depending upon the direction of the wave normal with respect to that of the magnetic field.

Following Appleton,[40] if we assume that friction is small, the index of refraction is given as a function of the frequency by

$$n^2=1+\frac{2}{2\alpha-\frac{\gamma_T^2}{1+\alpha}\pm\sqrt{\frac{\gamma_T^4}{(1+\alpha)^2}+4\gamma_L^2}} \tag{6}$$

[36] See footnotes 4, 5, 6, p. 16; 32, and 33, p. 19.
[37] See footnote 26, p. 18.
[38] Hartree, Proc. Cambridge Phil. Soc., vol. 27, p. 143.
[39] See footnotes 22, 23, 24, and 11, pp. 18 and 16.
[40] See footnotes 25, 26, and 27, p. 18.

where

$$\alpha = -\frac{m\omega^2}{4\pi Ne^2} - a$$

$$\gamma_L = \frac{m\omega\left(\frac{H_L e}{mc}\right)}{4\pi Ne^2}$$

$$\gamma_T = \frac{m\omega\left(\frac{H_T e}{mc}\right)}{4\pi Ne^2}$$

H_L and H_T are respectively the components of the earth's magnetic field along and at right angles to the wave normal for any direction of propagation with respect to the terrestrial magnetic field.

From this it is deduced that $n = 0$ when

$$1 + \alpha = 0$$

$$1 + \alpha = \pm\sqrt{\gamma_L^2 + \gamma_T^2} = \pm\gamma$$

From the equation $1 + \alpha = 0$ we have

$$f_c'' = \sqrt{\frac{N_{max}}{\pi}\frac{e^2}{m}} \quad \text{putting } a \text{ of eq. (3)} = 0$$

or

$$f_c'' = \sqrt{\frac{2}{3}\frac{N_{max}}{\pi}\frac{e^2}{m}} \quad \text{putting } a \text{ of eq. (3)} = \frac{1}{3}$$

when this ray just penetrates the layer. This is seen to be the critical frequency of the ordinary ray denoted by f_c''. Estimates of electron density on the basis of this critical frequency are seen to be independent of the earth's magnetic field.

From the roots involving γ we have for $a = \frac{1}{3}$

$$f_1' = \frac{-\frac{He}{2\pi mc} + \sqrt{\left(\frac{He}{2\pi mc}\right)^2 + 4\cdot\frac{2Ne^2}{3\pi m}}}{2}$$

$$f_2' = \frac{\frac{He}{2\pi mc} + \sqrt{\left(\frac{He}{2\pi mc}\right)^2 + 4\cdot\frac{2Ne^2}{3\pi m}}}{2}$$

or $f_2' - f_1' = \frac{He}{2\pi mc} = 1{,}455$ kc/s, assuming a value of H, the total terrestrial magnetic field, of 0.52 gauss for 180 km height at Washington.

It appears that there are two possible critical frequencies for the extraordinary ray. It will be seen, however, that the ray will ordinarily travel only until N is sufficiently large to return it, and it cannot therefore reach such an electron density as to cause f_1' to exist.

Then

$$f_2' = + \frac{\frac{He}{2\pi mc} + \sqrt{\left(\frac{He}{2\pi mc}\right)^2 + 4f_c^2}}{2}$$

Values of f_2' are plotted with respect to f_e'' for the F_1 layer in figure 1 and show the two frequencies, one which is called by Appleton the ordinary and the other the extraordinary ray which penetrate to the same electron densities. It can be seen that the critical frequencies for the two rays will also have this relation. The difference between values of f_e'' and f_2' is seen to approach a constant value of

$$1/2\left(\frac{He}{2\pi mc}\right)=728 \text{ kc/s} \quad .$$

at very high frequencies. It has also been shown that the two rays have different polarizations and are attenuated differently.[41]

From the foregoing, two methods of study of the ionosphere are suggested: (1) To observe the variations in virtual height and am-

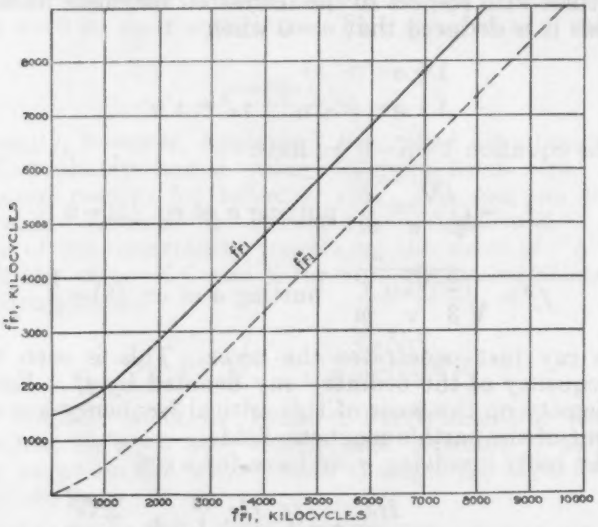

FIGURE 1.—*Graphs showing the frequency separation of the critical frequencies of the ordinary and extraordinary rays due to magnetic double refraction at 180 km height at Washington, D.C.* $f_F''{}_1$ *denotes ordinary ray critical frequency for* F_1 *layer.* f'_{F1} *denotes extraordinary ray critical frequency for* F_1 *layer.*

plitude at constant frequency as ionization or recombination occurs with changing time, and (2) to observe the variations in virtual height and amplitude as the frequency is changed so rapidly that variations with time can be neglected. This paper relates chiefly to results obtained by the second method.

For the successful application of this method, a large number of observations at various frequencies throughout the range in which reflections are returned must be made during a period so short that changes due to ionization or recombination are not very appreciable. Each transmission must be so selected, and be made so short that the probability of creating interference is negligible. It is possible to make sufficiently rapid measurements except during periods when violent changes are taking place in the layers.

In practice, the transmissions were limited to a minute or less, and the run through the portion of the spectrum in which reflections were

[41] Appleton and Builder, Proc. Phys. Soc., vol. 45, part 2, no. 247.

returned required from 30 to 60 minutes. In order to avoid missing any of the critical ranges, frequency changes must be made in steps of not more than 200 kc/s. Generally, the changes were made in steps of 100 kc/s or even less.

Because of the narrow frequency bands within which the critical frequencies occur, the transmitter used had a low-power oscillator of good frequency stability followed by a multi-stage amplifier which was keyed. Sufficient power is necessary to show small reflections occurring at critical frequencies through high atmospheric noise. The power was increased from time to time during the study until, at the last, somewhat more than 1 kw was in use. Single-wire horizontal high-angle radiators were employed.

A double-detection receiver having linear detector characteristics and operating a d-c amplifier of the bridge type was used to furnish the energy to an oscillograph galvanometer. The galvanometer was placed at the center of the bridge and had an electrical bias at all times, so that high resolution was possible. A light beam, reflected from the galvanometer, was projected from a three-sided rotating mirror and thence to a translucent celluloid screen. The triple-contact chopper at the transmitter and the rotating mirror at the receiver were rotated by means of synchronous motors operating from the same power supply. As the pulsing frequency was 3/2 times the line frequency, spurious noises, synchronous with line frequency, did not break the base line established by the galvanometer, and could be separated from pulses originating at the transmitter which do break this base line. Measurements of virtual height were made by bringing the beginning of each reflected pulse to a reference line. This was accomplished by rotating the motor frame through a known angle with a micrometer screw calibrated directly in kilometers. The ground, or reference pulse, was brought to a second reference line located ahead of the first to correct for the time of travel of the ground pulse.

Large variations in the amplitude of various reflections (frequently in the order of 1000 : 1 in field intensity) were found. No attempt was made to observe the relative amplitudes directly on the oscillograph screen. Instead a calibrated attenuator in the intermediate-frequency amplifier was used to reduce the amplitude of the pulse to a standard value for measurement, and the actual amplitude was determined from the attenuator setting. This method served several purposes: (1) It eliminated the effect of the second detector characteristic on comparisons of amplitude; (2) it corrected for the error due to the appreciable (though very small) time required for the transmitted pulse to rise from zero to full amplitude; and (3) it made possible the measurement of very small reflections.

As it was necessary to move the equipment during the period of these experiments, the transmissions were made over three different paths. The transmitting station was finally located at Beltsville, Md., with the receiving station directly south at Meadows, Md., 25 km distant. The ground path of the earlier transmissions was 20 km.

III. INVESTIGATIONS OF THE *E* LAYER

At the lower frequencies, reflections are returned from the *E* layer. The virtual height ranges consistently from about 100 km at frequencies in the broadcast band (550 to 1,500 kc/s) to about 120 km

at frequencies near the critical frequency. These heights do not vary much between day and night conditions. In the daytime the reflections at upper broadcast frequencies are very small or entirely missing, and are larger in winter than in summer. As the frequency is increased these reflections become very large in amplitude. In the neighborhood of the critical frequency, a number of phenomena usually are observed in the following order as the frequency is increased: (1) The virtual height increases rapidly to large values, (2) the amplitudes decrease rapidly, all reflections frequently disappearing entirely; (3) further increases in frequency cause a decrease in virtual height to *F*-layer values. Some variations of the character of these phenomena are observed from time to time, especially during periods when the absorption increases sufficiently to cause reflections to disappear.

This critical frequency is the lowest frequency which can pass through the *E* layer and is taken as a measure of the maximum

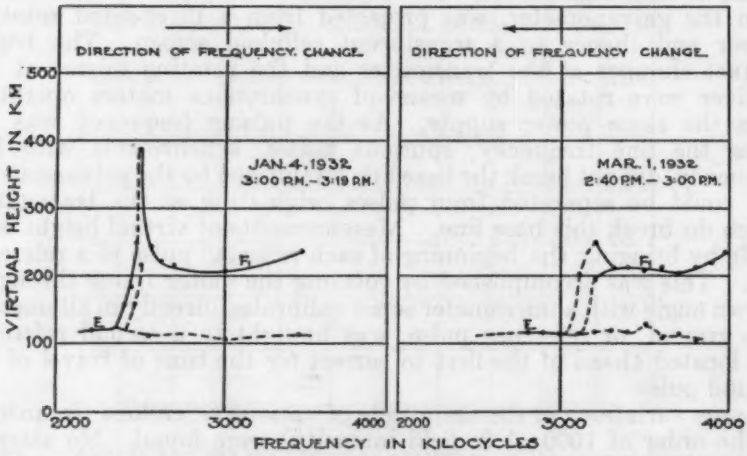

FIGURE 2.—*Typical cases of E layer critical frequency.*

ionization of the layer. It is termed the *E* critical frequency and here represented by the symbol f_E.

Typical cases of *E*-layer critical frequency are shown in figure 2. This phenomenon appears to be identical with that observed by Schafer and Goodall [42] and others, who held the frequency constant during a decrease in critical frequency due to recombination. The long retardation at critical frequency has been discussed by a number of writers,[43] [44] [45] and occurs when the frequency is just high enough to permit the pulse to pass through the layer.

Determinations of critical frequency are made by varying the frequency through the range in which these phenomena are observed. The results of a large number of determinations throughout the 2½-year period show that (with certain exceptions discussed later) the variation of f_E has certain quite regular characteristics during the daytime: (1) There is a regular diurnal variation, quite smooth,

[42] See footnote 16, p. 17.
[43] Appleton, Proc. Phys. Soc., vol. 42, p. 321, 1930.
[44] See footnote 17, p. 17.
[45] See footnote 27, p. 18.

f_E rising in the morning and falling in the afternoon; (2) the maximum occurs near local apparent noon, and the characteristic

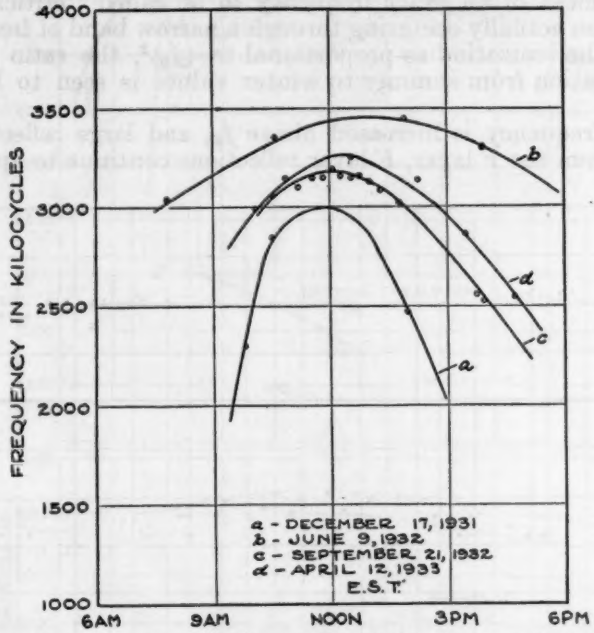

FIGURE 3.—*Typical diurnal variations of f_E selected for days during the various seasons.*

is quite flat during this period; (3) these noon-maximum-values have a seasonal variation, but very little day-to-day variation.

Figure 3 shows typical diurnal variations of f_E during selected days in each of the four seasons. Figure 4 shows a plot of a large number of values of f_E taken in the early afternoon, grouped around the dates indicated. These figures show the seasonal change in diurnal variation of f_E. Figure 5 shows the annual variation of the maximum values of f_E over an extended period. A few observations taken shortly after noon but corrected to noon by extrapolation from figure 4, are included.

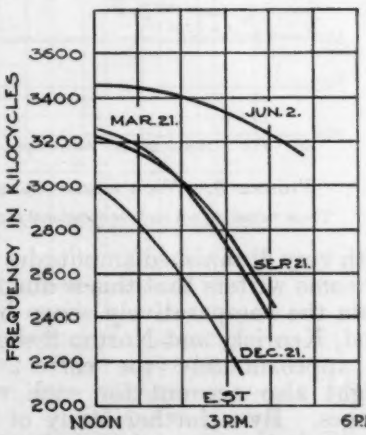

FIGURE 4.—*This figure shows graphs of a large number of E critical frequencies taken in the early afternoon and grouped around the dates indicated.*

From the regularity of the daytime diurnal and seasonal characteristics, it appears that the sun is the chief ionizing agency during the day. From these figures it can be estimated that the annual variation in noon maximum of f_E during this period was from about 3,000 kc/s in December to 3,400 kc/s in June. This estimate is subject to

certain limitations, in that daily observations were not made. There may also be slight differences in the opinions of various observers in the assignment of an exact frequency to be called "critical" for a phenomenon actually occurring through a narrow band of frequencies.

Taking the ionization as proportional to $(f_E)^2$, the ratio of maximum ionization from summer to winter values is seen to be about 1.3 to 1.

As the frequency is increased above f_E, and large reflections are returned from the F layer, E-layer reflections continue to appear but

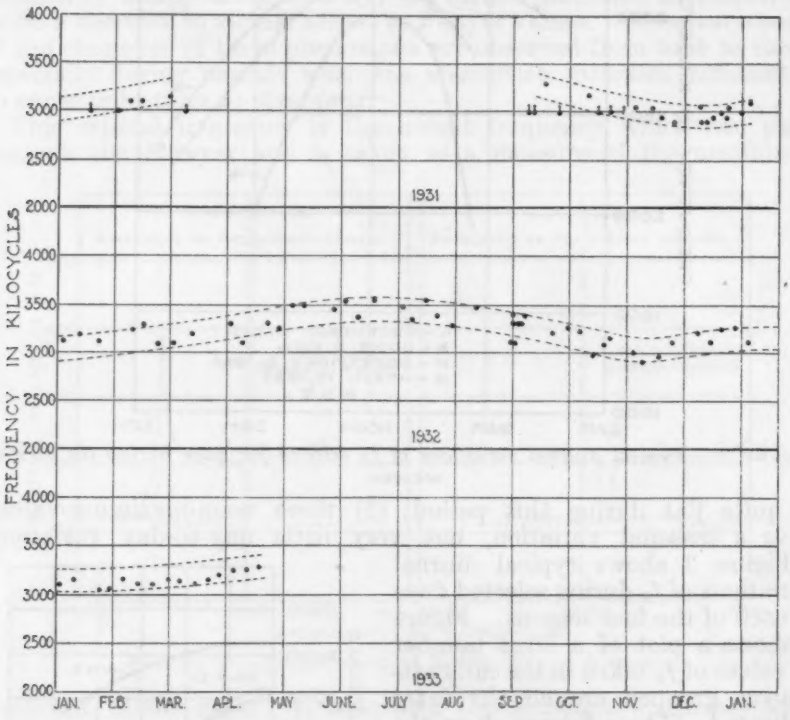

FIGURE 5.—*Noon maximum values of f_E for 1931, 1932, and 1933.*

These values do not include occasional random high values of ionization discussed in text.

with very diminished amplitudes. (See fig. 2.) It has been suggested by some writers that this is due to a small amount of energy reflected from the comparatively sharp boundary of the lower region. Gilliland, Kenrick, and Norton [46] show that the reflection coefficients are of approximately the correct magnitude. Magneto-ionic effects might also account for such reflections within certain frequency ranges. By a further study of these reflections it may be possible to obtain a more perfect understanding than now exists of the structure of this layer.

Occasionally reflections of great magnitude, sufficient to return a number of multiples, are returned from the E layer at frequencies

[46] See footnote 17, p. 17.

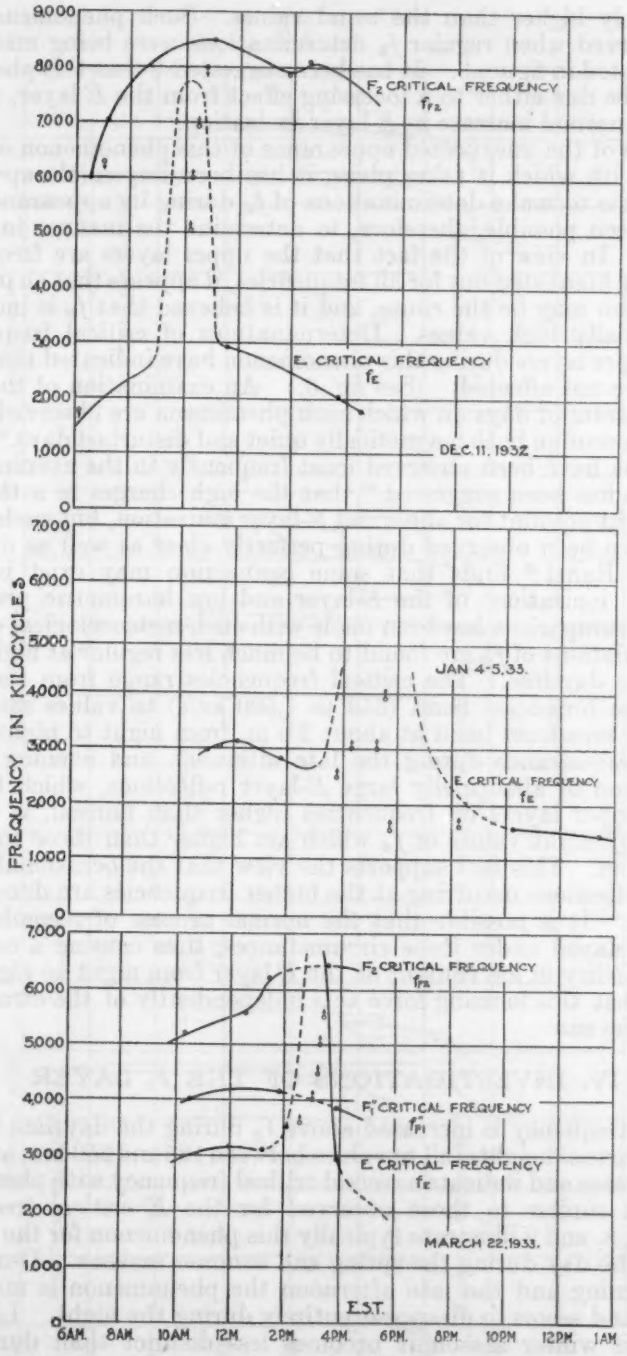

FIGURE 6.—*Examples of occasional random high values of f_E.*

0 indicates observations. ♂ indicates critical frequency is greater than observed frequency. ♀ indicates critical frequency is less than observed frequency.

considerably higher than the usual values. Such phenomena have been observed when regular f_E determinations were being made and are illustrated in figure 6. It has been suggested [47] that this phenomenon may be due either to a focussing effect from the E layer, or to a sudden abnormal increase in E-layer ionization.

Because of the unexpected appearance of this phenomenon and the rapidity with which it takes place, it has been impossible up to the present time to make determinations of f_E during its appearance. It has not been possible, therefore, to determine the manner in which f_E varies. In view of the fact that the upper layers are frequently completely blanketed out for all frequencies, it appears that an increase in ionization may be the cause, and it is believed that f_E is increased to abnormally high values. Determinations of critical frequencies for the upper layers during this phenomenon have indicated that these layers were not affected. (See fig. 6.) An examination of the magnetic character of days on which such phenomena are observed shows that they occur on both magnetically quiet and disturbed days.[48] The phenomena have been observed most frequently in the evening or at night. It has been suggested [49] that the high charges in a thunderstorm might account for abnormal E-layer ionization, but such occurrences have been observed during perfectly clear as well as overcast weather. Ranzi [50] finds that some connection may exist between these high ionizations of the E-layer and low barometric pressures. As yet no comparison has been made with such meteorological data.

The variations of f_E are found to be much less regular at night than during the daytime. The critical frequencies range from the lower part of the broadcast band (550 to 1,500 kc/s) to values somewhat above the broadcast band at about 2 a.m. from night to night. The frequent appearance during the late afternoon and evening of the phenomenon of abnormally large E-layer reflections, which blanket out the upper layers on frequencies higher than normal, is usually followed by night values of f_E which are higher than those found on other nights. This fact supports the view that the occasional strong E-layer reflections occurring at the higher frequencies are due to high ionization. It is possible that the normal process of recombination may be delayed under these circumstances, thus causing a considerable variability in ion content of the E layer from night to night. It appears that this ionizing force acts independently of the direct radiation of the sun.

IV. INVESTIGATIONS OF THE F_1 LAYER

As the frequency is increased above f_E during the daytime in summer, the virtual heights fall to values between 185 and 250 km, and then again increase and indicate a second critical frequency with phenomena somewhat similar to those observed for the E critical frequency. Figures 7, 8, and 9 illustrate typically this phenomenon for the various times of the day during the spring and summer seasons. During the early morning and the late afternoon the phenomenon is much less distinct, and seems to disappear entirely during the night. Likewise, during the winter season it becomes less distinct than during the

[47] Schafer and Goodall, Proc.I.R.E., vol. 20, p. 1131, 1932
[48] See footnote 27, p. 18.
[49] C. T. R. Wilson, Proc.Phys.Soc., vol. 37, p. 32D, 1924.
[50] Ranzi, Nature, vol. 130, p. 369, Sept. 3, 1932.

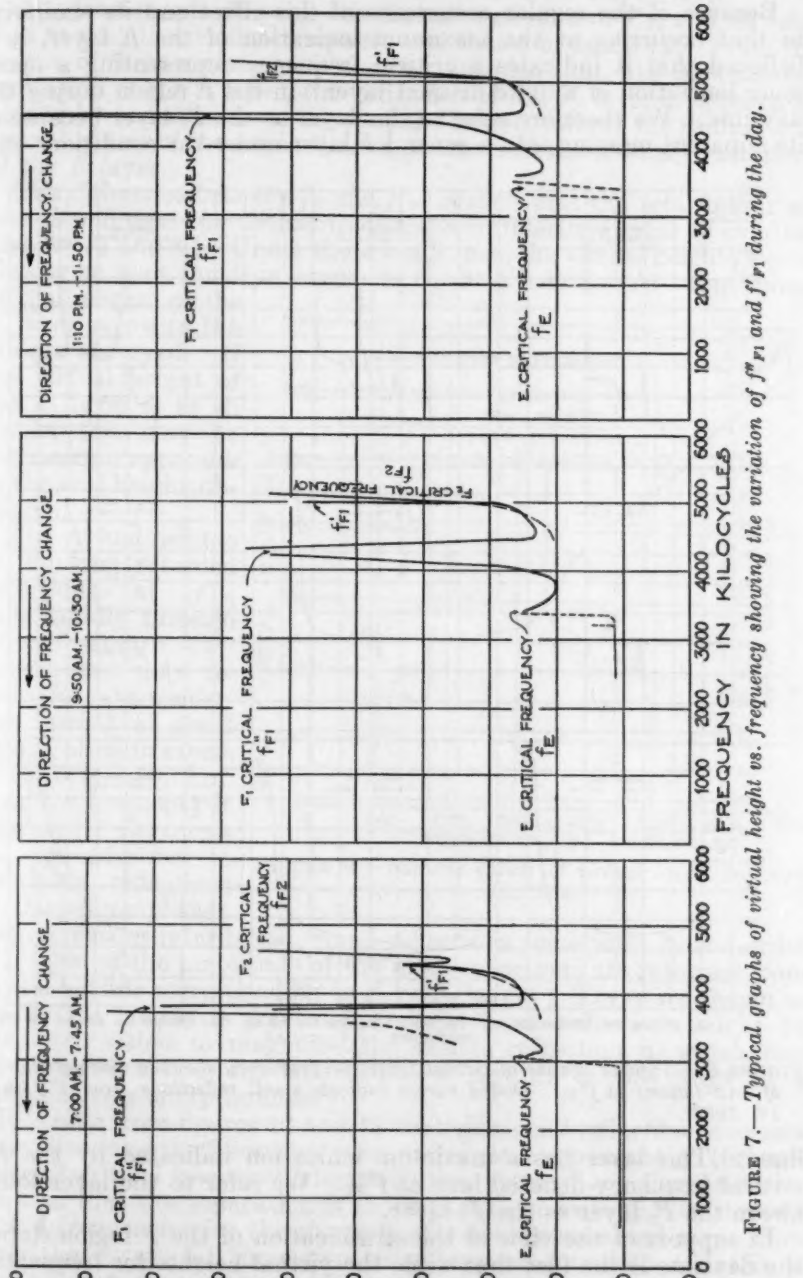

FIGURE 7.—*Typical graphs of virtual height vs. frequency showing the variation of* f''_{F1} *and* f'_{F1} *during the day.*

summer. Figure 10 illustrates this seasonal change during the afternoon.

Because of the regular occurrence of this effect and its similarity to that occurring at the maximum ionization of the E layer, it is believed that it indicates a critical frequency representing a maximum ionization of a quite distinct layer[31] in the F region during the daytime. We therefore refer to this layer as the F_1 layer because of its apparent merging into a general F layer under the conditions out-

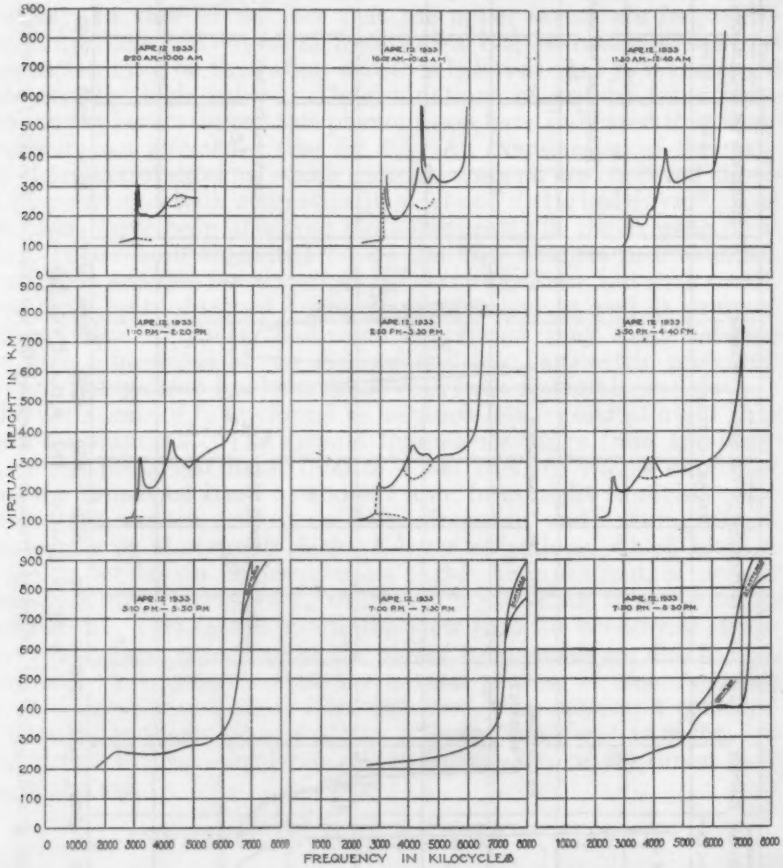

FIGURE 8.—*Typical graphs of virtual height vs. frequency showing diurnal changes of retardations at f''_{F1}. Dotted curves indicate small reflections from F'_1 (Apr. 12, 1933).*

lined. This layer has a maximum ionization indicated by the F_1'' critical frequency denoted here as f''_{F1}. We refer to the layer found above the F_1 layer as the F_2 layer.

In support of the view of the stratification of the F region during the daytime is the fact that while the virtual heights for frequencies less than f''_{F1} show no direct relation to the variation of the virtual heights of the F_2 layer, the virtual heights for these same frequencies take on a direct relation to F_2 layer heights when f''_{F1} has fallen below

[31] Eckersley, J.I.E.E., vol. 71, p. 405, 1932.

them. This indicates a separate F_1 layer whose ionization screens waves of frequencies below its critical value from the F_2 layer.

A typical graph showing the diurnal variation of f''_{F1} and its relation to the other critical frequencies is shown in figure 11. From the nature of these variations, it can be concluded that, like the ordinary ionization of the E layer, the ionization of the F_1 layer is apparently caused by radiation from the sun, and largely follows the diurnal and annual phases of the sun in the same manner as the ordinary variations of the E layer.

The difference between f_E and f''_{F1} is such that the retardation effects found near the critical frequencies ordinarily appear to overlap. (See figs. 7 and 8.) Under these conditions, the virtual heights would always be very much in excess of the real height. At some times, virtual heights of the F_1 layer as low as 185 km are observed. If the virtual height of the F_1 layer is at all stable, this may be the nearest approach to the real height obtained.

The virtual heights of the long retarded reflections at f''_{F1} vary rapidly through small frequency ranges, but may remain for a considerable period at great values, often in excess of 1,200 to 1,500 km.

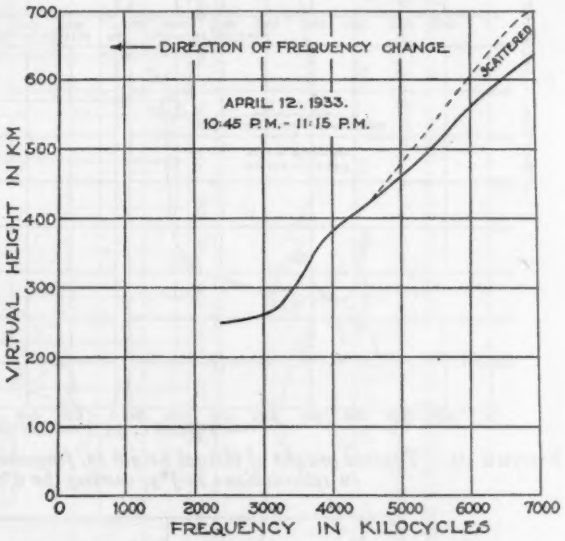

FIGURE 9.—*Evening values of virtual height for Apr. 12, 1933.*

As the frequency is increased through f''_{F1}, in addition to the main reflections of large amplitude and increasing retardation, small reflections sometimes in the order of 1/1,000 of the amplitude of the main reflections are returned from virtual heights corresponding to F_1 or F_2 layers. These are shown as the dotted curves in figures 7 and 8. Such reflections might be attributed either to magneto-ionic double refraction in which this reflection represents the extraordinary ray, or to the effect of a comparatively sharp boundary.

It is seen from figures 12 and 13 that this small reflection increases in amplitude as the frequency is increased, and appears to go through a second critical frequency about 800 kc/s above f''_{F1}. From figure 1 it is seen that this separation is about that to be expected for the two critical frequencies for the magnetically doubly refracted rays. Because the curves for these two reflections are found to maintain a fixed relation, it seems probable that they are due to magnetic double refraction in the F_1 layer, and that the second component is the extraordinary ray F'_1, having a critical frequency of f'_{F1}. The smaller amplitude of the extraordinary ray is probably due to the difference

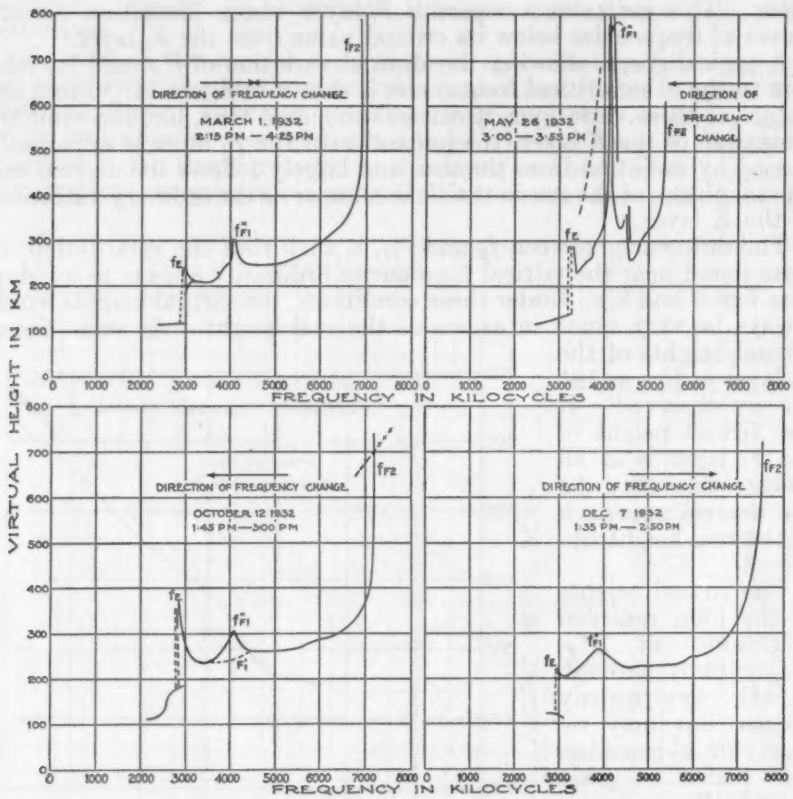

FIGURE 10.—*Typical graphs of virtual height vs. frequency showing seasonal changes in retardations at f''_{F1} during the afternoon.*

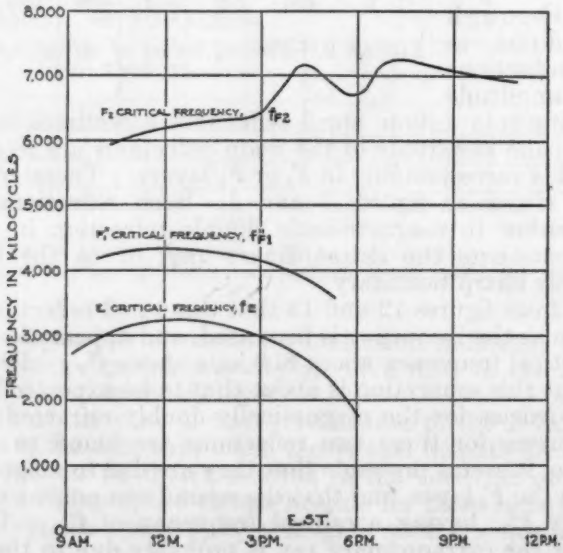

FIGURE 11.—*Typical diurnal variations of f''_{F1} showing its relation to other critical frequencies.*

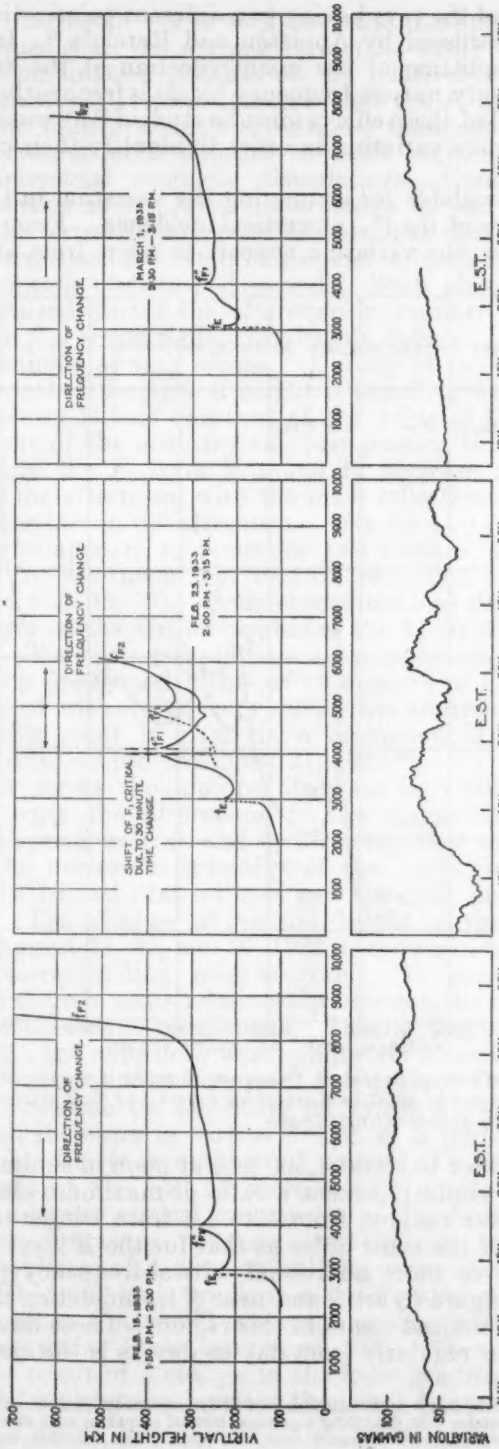
VIRTUAL HEIGHT IN KM
VARIATION IN GAMMAS
E.S.T.
DIRECTION OF FREQUENCY CHANGE
FEB. 15, 1933 1:50 P.M. — 2:30 P.M.
SHIFT OF f_1 CRITICAL DUE TO RAPID TIME CHANGE
FEB. 23, 1933 2:00 P.M. - 3:15 P.M.
MARCH 1, 1933 2:30 P.M. — 3:18 P.M.

FIGURE 12.—*Graphs showing virtual height vs. frequency for magnetically quiet and disturbed days.*

Magnetograms for corresponding times are shown at bottom of figure. Center figure shows the two magnetically doubly refracted rays.

in the absorption of the rays having two different polarizations. This effect has been discussed by Appleton and Ratcliffe.[52] In addition to these effects, splitting of the main reflection at the critical frequencies through very narrow frequency bands is frequently observed. It appears that all of these effects must be studied [53] by some means of continuous frequency variation in order to identify their cause more positively.

Few data are available for estimating the variation in the diurnal and seasonal values of the f''_{F1} at vertical incidence. From the available data, however, the variation appears to range from about 3,800

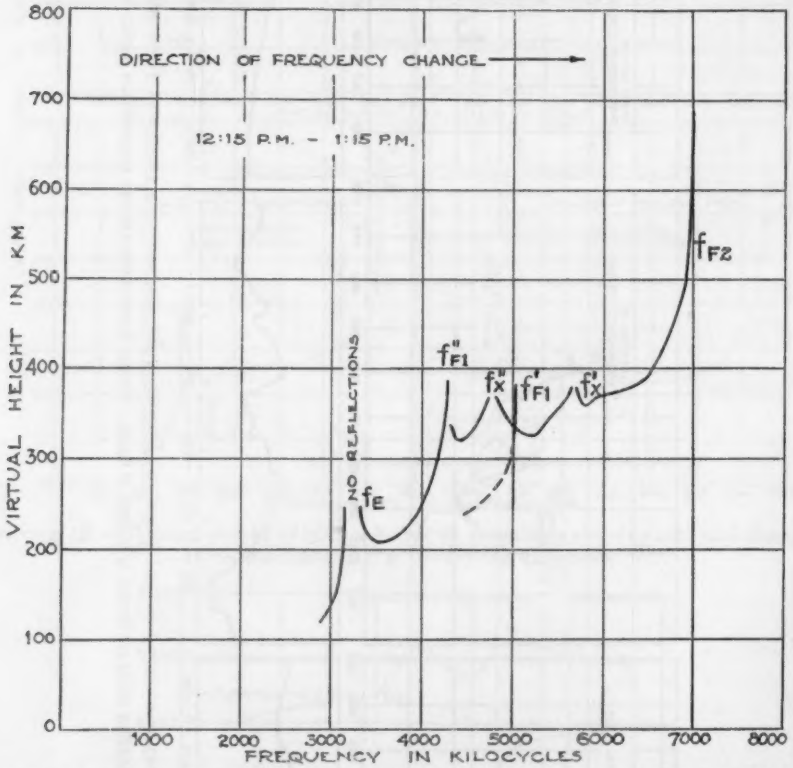

FIGURE 13.—*Graph of virtual height vs. frequency showing a number of critical frequencies due to existence of additional irregular layers and their critical frequencies for both magnetically double-refracted rays.*

kc/s at noon in winter to about 4,500 kc/s at noon in summer. From equation (4) this would represent a ratio of maximum electron density for the F_1 layer ranging from 1 to 1.4 from winter to summer. This variation is of the same order as that for the E layer.

Frequently one or more additional critical-frequency phenomena such as shown in figure 13 are found near f''_{F1}, indicating the appearance of additional ionized strata in this region. These have not been observed to appear regularly from day to day as is the case with the

[52] See footnote 28, p. 18.
[53] See Note on a Multi-Frequency Automatic Recorder of Ionosphere Heights, T. R. Gilliland, B.S. Jour. Research (RP608), October 1933, describing a practical method of making such observations.

layers just discussed. It is seen that the disappearance of the F_1 critical frequency in the evening cannot be easily explained on the basis of recombination because of the relatively slow decrease in critical frequency. It seems possible that the F_1 and F_2 layers may drift together to form a single layer under these conditions.

Some correspondence appears to exist between phenomena at f''_{F1} and terrestrial magnetic disturbances. Comparisons of the pulse retardation at f''_{F1} with disturbances in the horizontal component of the terrestrial magnetic field indicate that during disturbed periods retardations are often longer and subject to greater absorption than during undisturbed periods. Such phenomena are most easily recognized during the afternoon in summer or at midday in winter when f''_{F1} is not ordinarily sharply defined. Figure 12 shows a typical example of such a case. A study of the long retardations of f''_{F1} shows that the virtual height is usually greatest about noon. If the frequency is held constant at the value of the noon f''_{F1}, the virtual height of the ordinary ray just passing through the F_1 and reflected from the F_2 layer is found to decrease nearly uniformly throughout the afternoon, with the main reflections joining with the F'_1 reflections late in the afternoon. (See fig. 14.) This decrease in virtual height appears to occur for two reasons: (1) Reduction in f''_{F1} during the afternoon (fig. 10); (2) reduction in the retardation of pulses at f''_{F1} (fig. 8). Both causes tend to decrease the effect of the F_1 layer on the virtual heights of the F_2 layer as the afternoon progresses. The long retardations accompanying f'_{F1} disappear as the afternoon progresses. This effect appears to be independent of the decrease of critical frequency during the afternoon. Information regarding this point is given in a discussion of results obtained during the solar eclipse of August 31, 1932.[54]

Figure 14 shows the uniform decrease in virtual height which occurred during the afternoons of the magnetically undisturbed periods of September 1, 3, and 4, 1932, together with the magnetograms of the horizontal intensity of the terrestrial magnetic field taken by the United States Coast and Geodetic Survey at Cheltenham, Md. The change of virtual height during the disturbed periods of August 27, 29, and 30, 1932, is shown in figure 15, together with the corresponding magnetograms. It appears from these curves that there is some relationship between the magnetic changes and the virtual-height phenomena. During the major disturbance on August 27, the reflections were completely absent for long periods, apparently on account of abnormal absorption. During the periods of great retardation on the other disturbed days, reflections were small. Such increases in virtual height at a frequency just above f''_{F1} might be due to a number of causes: (1) An increase in the virtual height at f''_{F1}; (2) an increase in f''_{F1}; (3) the existence of one or more higher critical frequencies in the F_2 region which pass through this frequency as they decrease due to recombination; (4) the appearance of a new critical frequency slightly higher than f''_{F1} due to changing ionic gradient in the F_2 layer.

An increase in f''_{F1} would represent an increase in ionization of the F_1 layer under these conditions. (1), (3), and (4) might all occur as the result of a change in the ionic gradient of the F_1 layer or of unusual ionic strata between the usual F_1 and F_2 layers.

[54] Kirby, Berkner, Gilliland, and Norton. B.S.Jour. Research, December 1933.

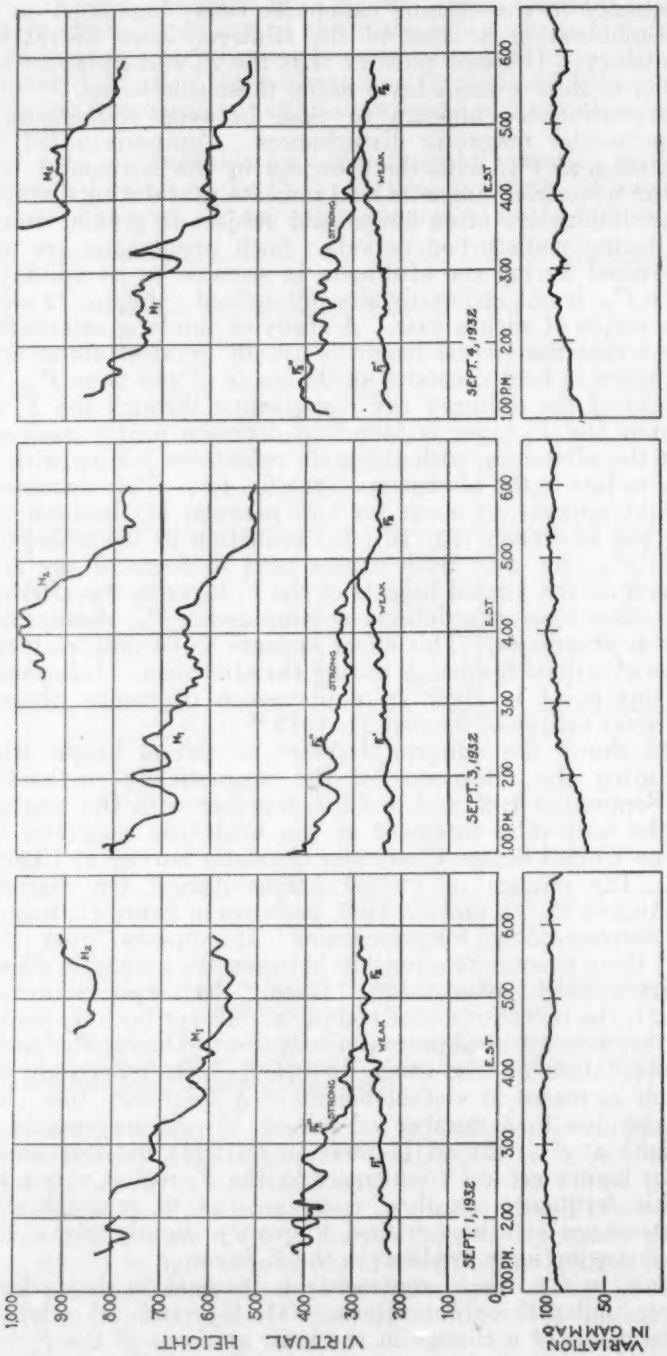

FIGURE 14.—*Graphs showing decrease in retardation of F_2 reflections on 4,200 kc/s as afternoon progresses.*

The retardation is produced by passing through the F_1 layer at a frequency just above f'_{F_1}. The magnetograms of horizontal intensity of the earth's field are also shown for magnetically quiet days.

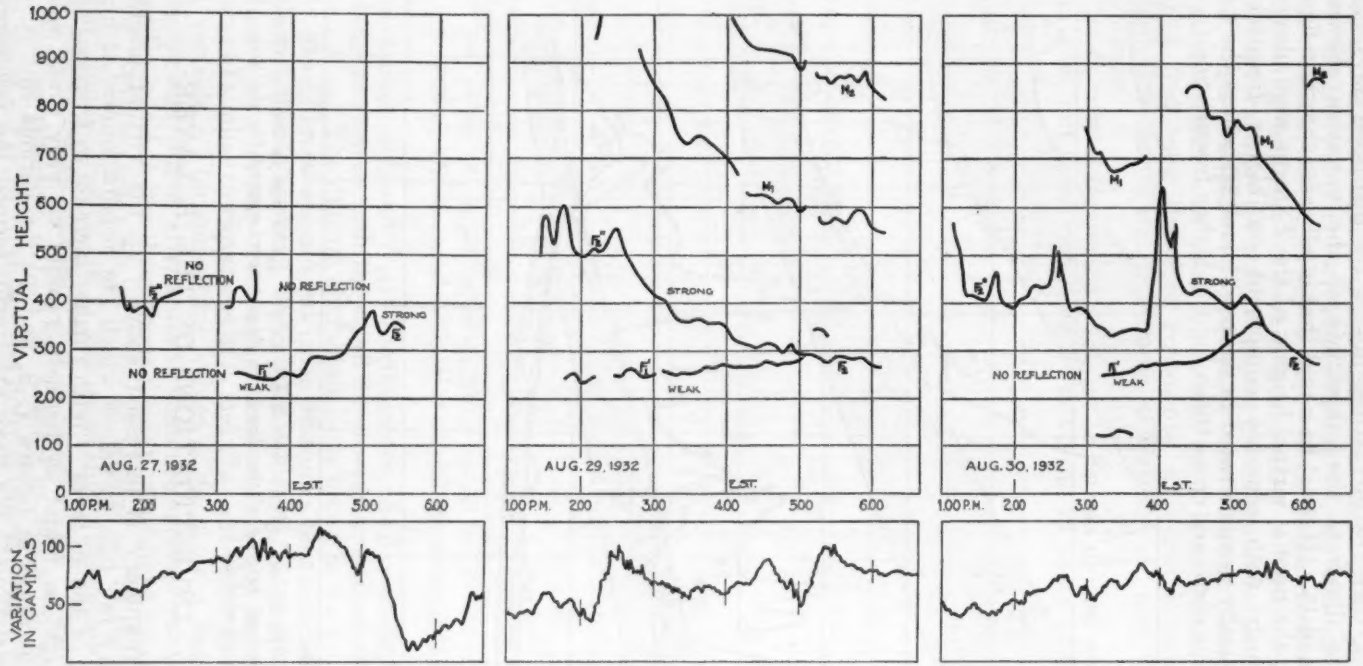

FIGURE 15.—*Graphs showing decrease in retardation of F_2 reflections on 4,200 kc/s as afternoon progresses.*

The retardation is produced by passing through the F_1 layer at a frequency just above f''_{F1}. The magnetograms of horizontal intensity of the earth's field are also shown for magnetically disturbed days.

Figure 16 shows the envelopes of the virtual heights for the undisturbed days, with the virtual heights for the disturbed days superimposed, to illustrate the magnitude of the variation shown in figures 14 and 15. It must be noted that in all cases shown in figures 14 and 15, the normal virtual heights of the F_2 layer were observed simultaneously with separate equipment on higher frequencies. This is typically demonstrated in figures 21 and 22, where the 4,000 to 4,300 kc/s contours cross those for the higher frequencies.

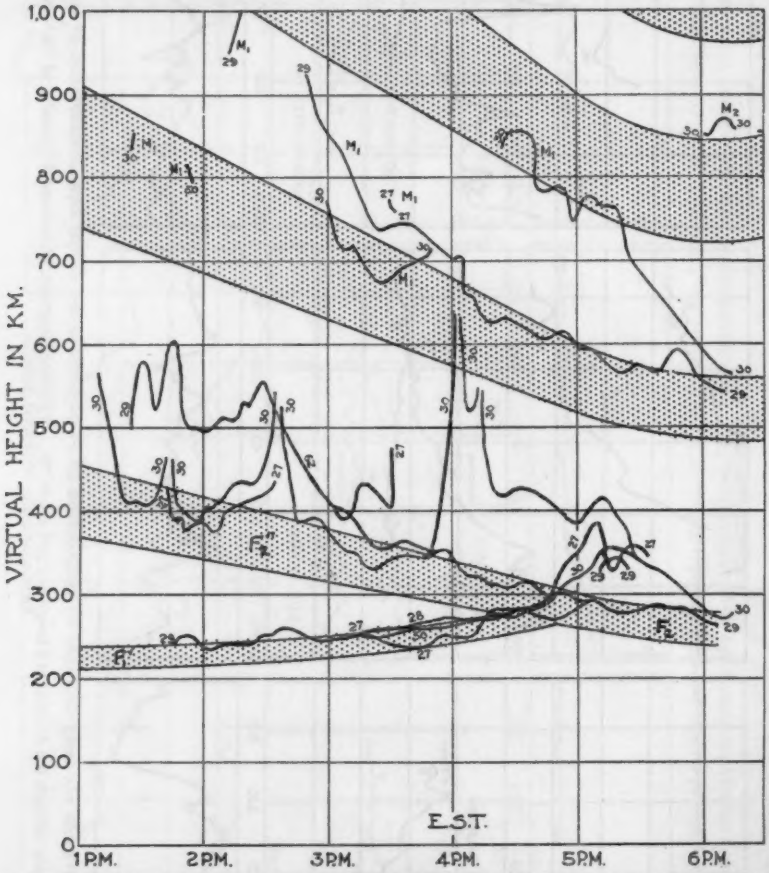

FIGURE 16.—*Envelopes of the virtual heights for 4,200 kc/s for undisturbed days, with the virtual heights of the disturbed days superimposed for the days shown in Figures 14 and 15.*

V. INVESTIGATIONS OF THE F_2 LAYER

As the frequency is increased above f''_{F1}, the virtual height of the ordinary ray falls to values which are usually somewhat higher than those of the F_1 layer. With further increase in frequency, the virtual height is found to increase rapidly to very great values. This is illustrated in figures 7, 8, and 10 for various diurnal and seasonal variations. We have arbitrarily termed the frequency at

which the maximum slope of this sudden increase in height takes place as the F_2 critical frequency, and denoted this frequency as f_{F2}.

As the frequency is increased through f_{F2}, the reflections become rapidly smaller in magnitude as the virtual height increases, finally disappearing entirely. Above this frequency either no reflections at all are returned, or the reflections are greatly retarded and extremely small, and variable in magnitude and virtual height. These "scattered reflections" are discussed in a later section. The F_2 critical frequency therefore represents, at vertical incidence, the highest frequency which returns reflections of any appreciable magnitude.

The F_2 critical frequency is subject to certain diurnal and seasonal variations, but these variations do not occur in phase with, or in the

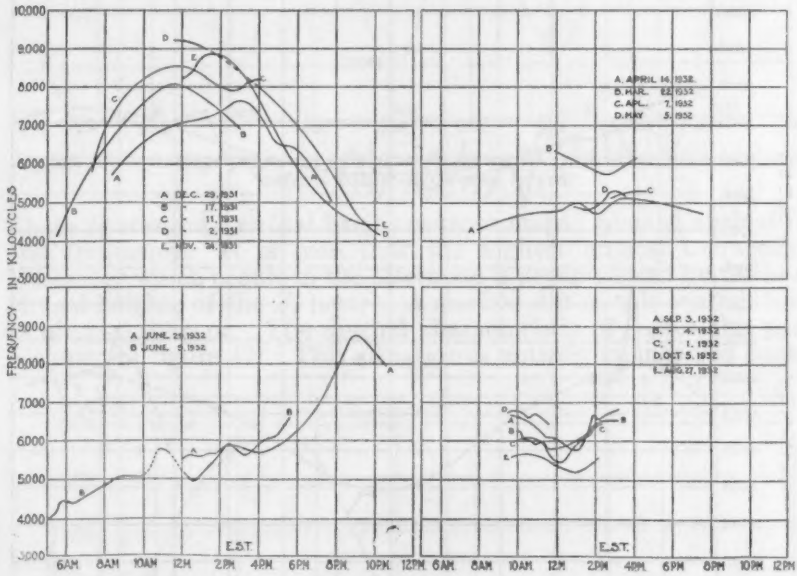

FIGURE 17.—*Seasonal variation of diurnal characteristic of* f_{F2}.

same manner as f_E and f''_{F1}. Furthermore, the day-to-day variations are large compared with the small day-to-day variations observed for f_E and f''_{F1}. The diurnal characteristic is found to vary quite differently for different seasons. Figure 17 shows this seasonal variation in diurnal characteristic. The winter values of f_{F2} are seen to have a diurnal characteristic reaching a maximum about noon. This is somewhat similar to variations in f_E and f''_{F1}, but much more irregular and variable. The springtime values of f_{F2} show a flatter diurnal characteristic, falling after sunset; while the summer values of f_{F2} are generally found to rise throughout the day, reaching a maximum after sunset. The retardations at f_{F2} for all seasons are of the same order of magnitude. (See fig. 10.) Figure 18 shows the seasonal and day-to-day variation in noon and 2 p.m. values of f_{F2}. Figure 19 shows the average variation during the 4 years in which the observations were made. Figure 20 shows the diurnal characteristic for a winter day on which f_{F2} was high.

Several important experimental facts are to be obtained from these data:

(1) The values of f_{F2} are higher at midday in winter than at midday during the summer by a large factor. This is distinctly the reverse of the trend of f_E and f''_{F1}.

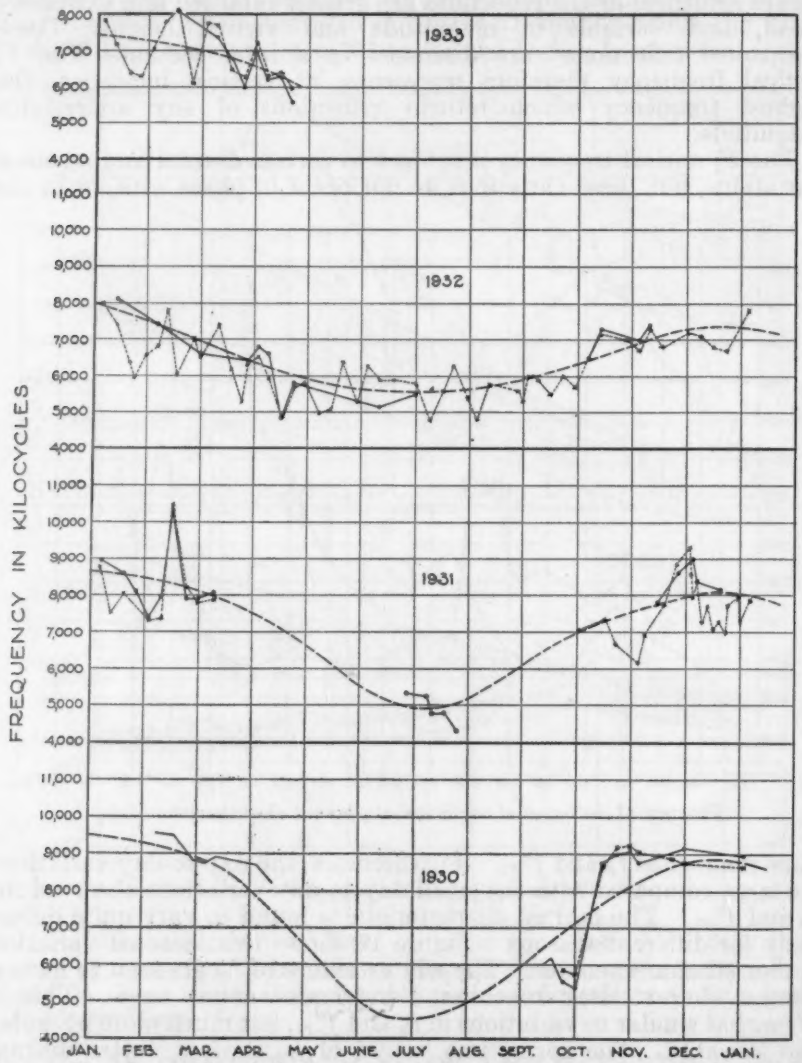

FIGURE 18.—*Seasonal and day-to-day variation in noon and 2 p.m. values of* f_{F2}. ——— *noon* – – – *2 p.m.*

(2) The values of f_{F2} reach a maximum some time near noon in the winter, but usually somewhat after sunset in the summer, while the values of f_E and f''_{F1} regularly reach a peak at noon throughout the year.

(3) The values of f_{F2} vary widely from hour to hour and from day to day, while values of f_E and f''_{F1} for the same time vary only slightly.

(4) The values of f_{F2} do not show a symmetry of diurnal characteristic about noon for all seasons as do those of f_E and f''_{F1}.

The characteristic diurnal changes in virtual heights are shown in figure 21 for December 21, 1932, and in figures 22 and 23 for April 5 and 12, respectively. (See fig. 8 for additional data on fig. 23.)

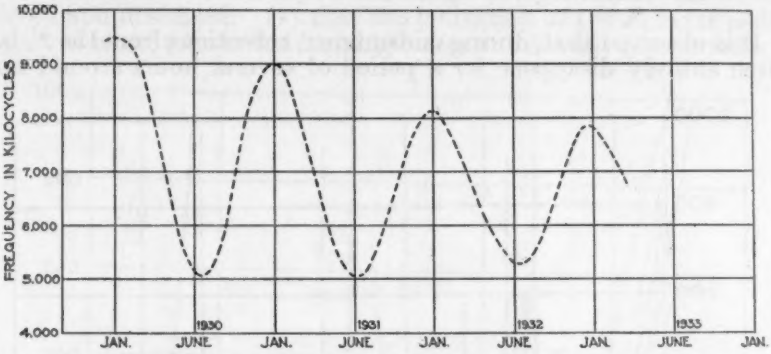

FIGURE 19.—*Average variation as shown in figure 18, plotted to indicate change in average values from year to year.*

These figures are "virtual height contour maps" plotted against time and frequency. It is seen that the highest critical frequency in December which occurs in the afternoon is accompanied by the lowest virtual heights of the F_2 layer. A marked dip in this contour occurs at about 1:30 p.m. The diurnal characteristic of f_{F2} for this period is shown in figure 17. This situation is entirely changed as summer

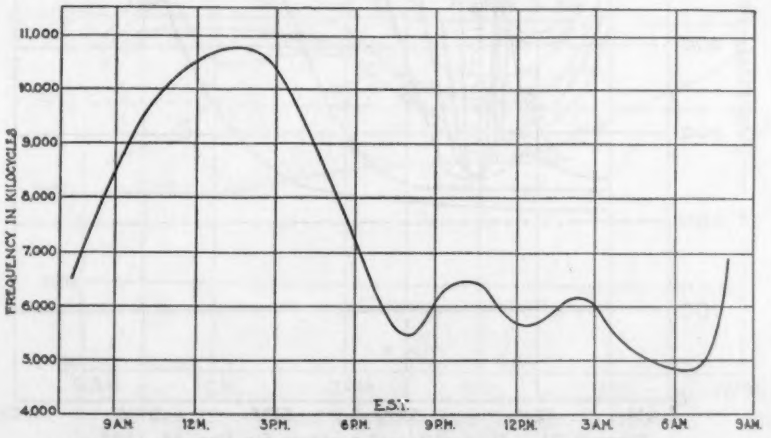

FIGURE 20.—*Diurnal characteristic for a winter day of high f_{F2}.*

approaches, as is seen from figures 22 and 23. Here f_{F2} (shown in fig. 8 for fig. 23) has a peak in the evening at about 7:30 p.m. during April, and the contours show a definite dip in the virtual height at this time. In addition, the irregular hour-to-hour variations of f_{F2} appear in the contours.

In general, the diurnal characteristic just discussed changes with season, the major dip in the contours, with the accompanying highest

critical frequency, occurring latest in the evening in midsummer. This brings out another important fact:

(5) The lowest virtual heights of the F_2 layer for all frequencies at which reflections are returned usually occur at about the same time as does the maximum f_{F2}, irrespective of the time of day at which this occurs. A study of figures 12–21 also serves to illustrate this fact.

It is observed that, during midsummer, reflections from the F_2 layer often entirely disappear for a period of several hours around noon.

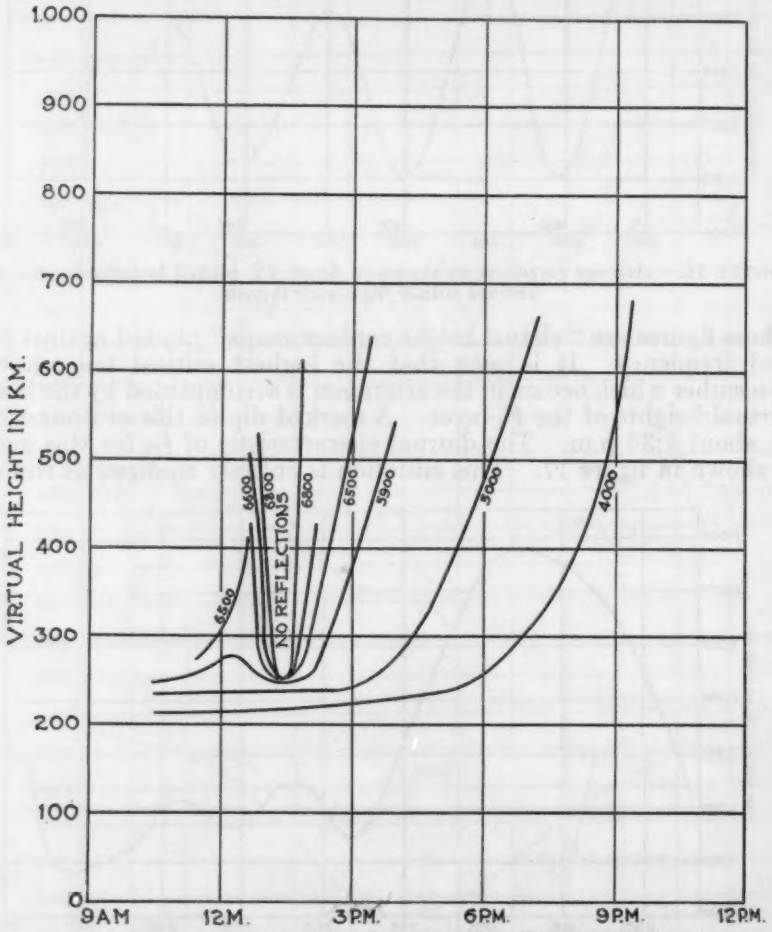

FIGURE 21.—*Virtual hieght contours for Dec. 21, 1932.*

This disappearance is preceded by a very marked reduction in intensity, and it seems that the reflections finally disappear entirely without a decrease in f_{F2} through the frequency range in which reflections were previously returned from the F_2 layer.

It will be seen that while the maximum ionizations for the E and F_1 layers generally follow the seasonal and diurnal variations of the sun, f_{F2} shows the following major deviations from this form of variation. From our observations, (1) the maximum value of f_{F2} bears no fixed

relation to the altitude of the sun during any season, (2) the maximum noon value of f_{F2} occurs when the south declination of the sun is the greatest, (3) when the north declination of the sun is the greatest, the maximum f_{F2} occurs after sunset.

It is apparent that f_{F2} is subject to effects not evident in the case of the lower layers. Several possible causes of such effects will be considered and discussed. (1) that the ionization of the F_2 layer is due, in part at least, to external ionizing forces not directly associated with

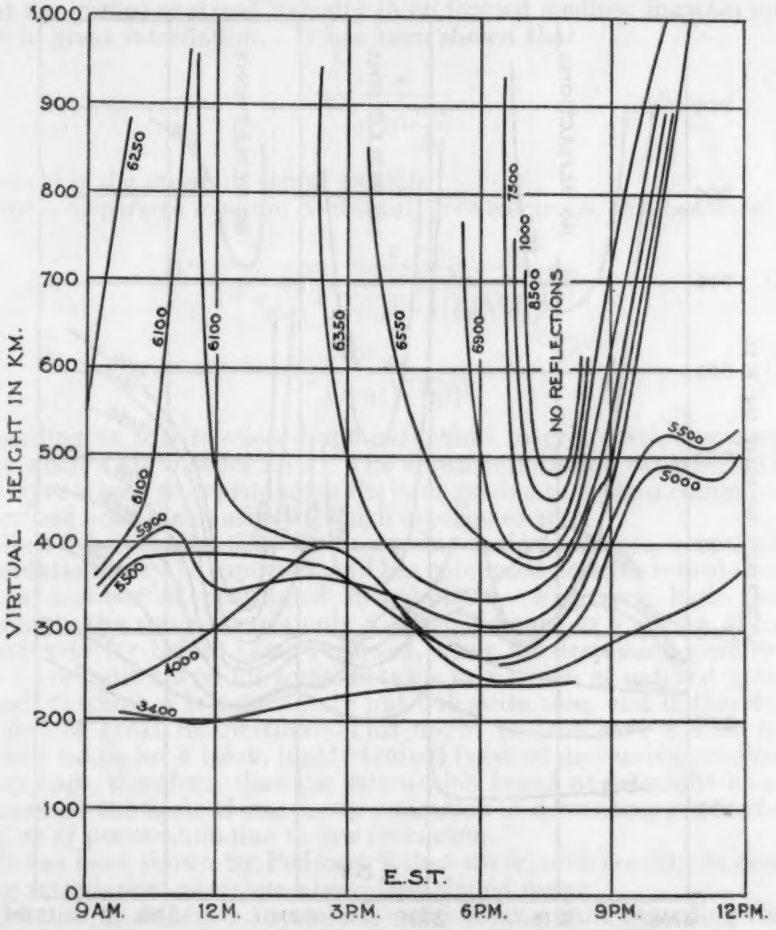

FIGURE 22.—*Virtual height contours for Apr. 5, 1933.*

the sun, (2) that ionization of the F_2 layer is due, in part, to drift of electrons from other ionized regions, and (3) that the variations of f_{F2} depend upon absorption and not upon ionization, at least during those parts of the day in which the deviations occur, when the ionization is associated with the sun in the same manner as that of the lower layers.

We will discuss the reasonableness of these possible causes in the light of the data at hand.

The fact that the ionization of the F_2 layer has a diurnal variation which is associated with the solar day would seem to indicate that the origin of the ionization is solar rather than cosmic.

A possible drifting together of the F_1 and F_2 layers so as to form a single layer has been mentioned. Such a drift would appear to be a comparatively slow process, but it might be possible to obtain a concentration of ions in this manner. Rapid changes in f_{F2} might be explained on the basis of a nonuniform and changing horizontal dis-

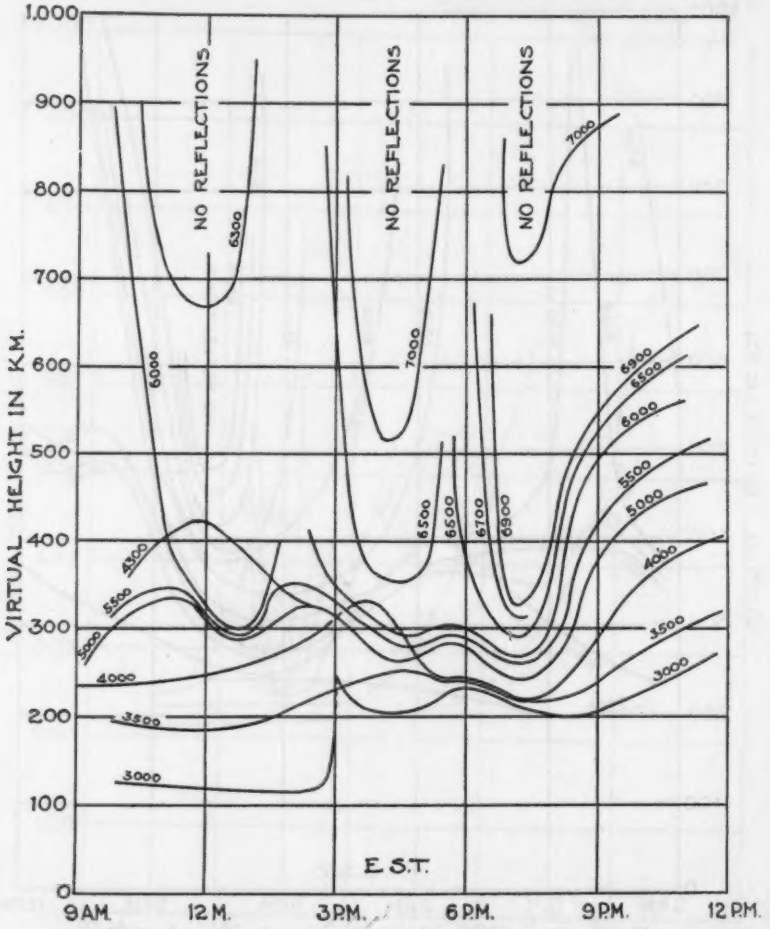

FIGURE 23.—*Virtual height contours for Apr. 12, 1933.*

tribution of ions in the F_2 layer. It is difficult, however, to account for the lower ionization in the summer day than in the winter day on such a basis unless there are rather large and complex changes in atmospheric distribution with season.

If we assume that the chief source of ion concentration in the F_2 layer is direct radiation from the sun, as seems to be the case with the lower layers, our conception and definition of f_{F2} cannot be the same as that given for the critical frequencies of the lower layers.

Critical frequency has been defined for the E and F_1 layers as the lowest frequency at which waves penetrate these layers, and it therefore serves as a measure of the maximum ionization of these layers. If, as might be expected, the maximum ionization for the F_2 layer takes place about midday throughout the year, we must consider, during the summer daytime at least, that f_{F2} depends upon absorption rather than upon penetration. We will therefore discuss this possibility.

As has been previously mentioned, a number of authors have shown that the group, or signal, velocity in an ionized medium may be subject to great retardation. It has been shown that

$$u = \frac{c}{n + \omega \frac{dn}{d\omega}} \tag{7}$$

where u is the group or signal velocity.

For a dispersive medium containing free electrons, this becomes:

$$u = \frac{c}{n + \omega \frac{d}{d\omega}\left(1 - \frac{4\pi Ne^2}{m\omega^2 + a(4\pi Ne^2)}\right)^{1/2}} \tag{8}$$

$$= \frac{cn}{1 - a(1-n^2)^2} \tag{9}$$

According to this relation, large reductions in group velocity occur only when n approaches zero. The actual retardation experienced in the layer is seen to depend upon the ionic gradient for the medium just described near the density at which n becomes zero.

Breit [55] has shown that for decreasing ionic gradients, very great retardations may be expected, and has computed possible retardations for a number of postulated distributions. For very high ionic gradients the wave travels only a short distance in a region of low group velocity before being returned, while for decreasing gradients the wave must travel for some distance in a region of reduced group velocity, where n is very nearly but not quite zero, and is therefore subject to great retardation. This might be true over a wide frequency range for a thick, highly-ionized layer of decreasing gradient. It appears, therefore, that the retardation found at f_{F2} might be explained on the basis of increasing ionization of decreasing gradient as well as of penetration due to low ionization.

It has been shown by Pedersen [56] that when such conditions cause long retardation, complete absorption should occur.

Because of difficulty in making valid assumptions regarding conductivity and resulting absorption under these conditions, we will refer to experimental data to determine the possibility of complete absorption due to such electron distribution. A case of this sort of complete absorption which can be positively identified in the presence of a higher reflecting stratum is shown in figure 15 for August 27, 1932. Here the reflections at 4,200 kc/s were completely absent for an extended period due to conditions in the F_1 layer while at frequencies as much as 1,500 kc/s higher good reflections were returned. The

[55] Breit, Proc.I.R.E., vol. 17, p. 1508, September 1929.
[56] Pedersen, P. O., Proc.I.R.E., vol. 17, p. 1750, October 1929.

value of f_{F2} for this period is shown in figure 17. Such cases are frequently observed at critical frequencies and occasionally throughout bands of several hundred kilocycles no reflections are returned. A study of the data shows that when the virtual height of a layer changes only slowly with frequency, the reflection strength and the number of multiples is the greatest. The reflections become small and the multiples disappear when the virtual height changes rapidly with frequency. Great virtual heights occurring at critical frequencies are usually associated with high absorption.

From this it seems possible that above f_{F2} there may be complete absorption as well as long retardation, the ionization increasing continuously but with a decreasing gradient. If some mechanism of this sort is assumed to limit the maximum frequency at which reflections are returned, f_{F2} then indicates a boundary above which the ionization gradient decreases sufficiently rapidly to cause long retardation and large absorption, rather than the maximum ionization in the F_2 layer.

It is believed that the observed data can be qualitatively explained in a satisfactory manner on this basis. During the winter day there may be comparatively high ionic gradients due to the low incidence of the ionizing radiation on this layer. During the summer, this radiation at a more nearly normal incidence may create a more diffuse layer due to its greater penetration, thus causing long retardation and high absorption over a wider band of frequencies until such time as recombination or ion drift at the bottom of the layer cause higher gradients to appear. At such a time the critical frequency may be expected to rise and the virtual heights decrease as shown in figures 20 and 21.

Observations at night frequently show one or more secondary increases in f_{F2} after the main increase, with corresponding decreases in virtual height. These secondary increases might be due either to small increases in ionization or to increased ionic gradients caused by recombination or changes of distribution of the ions in the layer. So far, it has not been possible to determine with certainty whether the phenomena associated with f_{F2} are due to penetration or absorption but the evidence leads to the belief that both factors may be involved. If this is true, f_{F2} frequently is not a measure of the maximum ionization of the F_2 layer.

From the foregoing discussion, it appears that the midday values of the F_2 ionization might exceed the values corresponding to the maximum value of f_{F2} by a considerable amount. On this basis it can be estimated from equation (4) with $a=0$ that this maximum ionization reaches 1.5×10^6 electrons per cm^3 frequently, and is known to be at least 2.5×10^6 electrons per cm^3 in the evening on certain occasions. With $a=1/3$ the corresponding electron densities are 2.25×10^6 and 3.75×10^6.

A study of the figures indicates that the heights of the F_2 layer may be estimated to be below 250 km. This estimate is based upon the same approximations as were mentioned in connection with the F_1 layer.

Compared with the fairly stable values of f_E and f_{F1} during the day, f_{F2} is subject to small rapid fluctuations superimposed upon its general diurnal characteristic. This results in rapid changes in virtual height such as shown in figure 24.

Because of the rapidity of these fluctuations, it is not valid to assume that time changes are negligible while working near f_{F2} with a single equipment. For this reason we hesitate to comment on such critical-frequency phenomena as are shown in figure 25. It is possible that such irregular changes occur with time more rapidly than the frequency can be changed. It is possible at least in the case of figure 25(*d*), however, that the two critical frequencies shown were both real, and that a temporary double stratification appeared in the F_2 layer during the first run, the higher stratum disappearing by the time of the second run thus leaving only the first critical frequency. Such phenomena have thus far been observed only during the summertime. Further evidence as to the possible variable stratification of the F_2 layer could be obtained by making simultaneous experiments with several equipments operating at different frequencies.

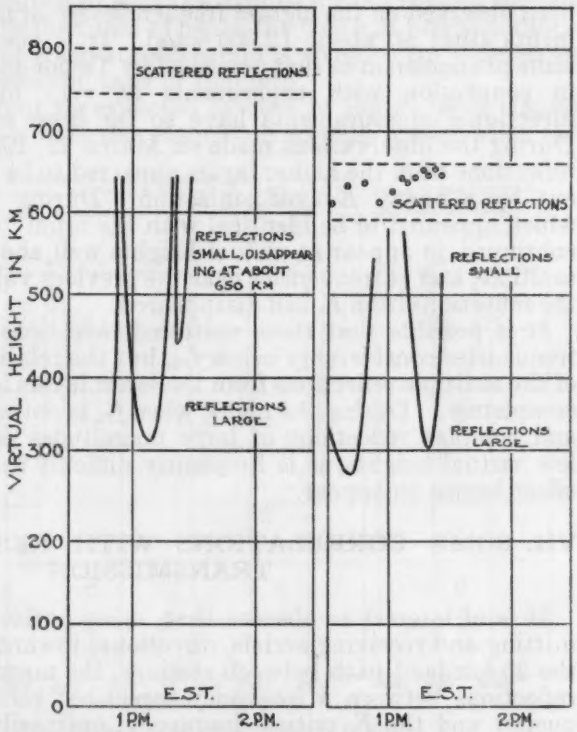

FIGURE 24.—*Characteristic variations in virtual height near f_{F2}. This shows rapid variation of f_{F2}.*

No obvious relation between magnetic disturbances and values of f_{F2} is apparent. Very high and very low values of f_{F2} are often observed during magnetic disturbances and seem to occur less frequently during undisturbed periods. Normal values of f_{F2} have also been observed during disturbed periods. If the values of f_{F2} are largely determined by ionic gradient and absorption, it is reasonable to expect that magnetic disturbances might produce effects not easy to interpret.

VI. SCATTERED REFLECTIONS

The "scattered reflections" mentioned as occurring above f_{F2}, appear to be of a nature quite distinct from the reflections previously discussed. These reflections are found to appear first at a frequency somewhat below f_{F2} and at a virtual height generally above 600 km. Their virtual height appears to be independent of changes in the

virtual height of the F_2 layer as shown in figure 22. The average virtual height increases slowly with frequency, often extending to above 1,000 to 1,500 km at frequencies well above f_{F2}. These are characterized by a small and variable amplitude, and a rapid variation, through a small range, of virtual height, best described as "rapidly popping in and out at various heights."

During F_2 critical frequency runs, as the virtual height of the F_2 layer was observed to increase rapidly, the F_2 reflection was usually completely absorbed before reaching the virtual heights of these scattered reflections, which were practically unchanged by small frequency variations in the winter. Scattered reflections have been observed on the highest frequencies so far used in these measurements (that is, about 12,000 kc/s). It is possible that this is the same phenomenon as that described by Taylor and Young [57] and others in connection with experiments at very high frequencies. No directional measurements have so far been made of their source. During the observations made on March 22, 1933, shown in figure 6, reflections from the higher layers appeared to be completely blanketed out by a heavy E-layer ionization. During this time, reflections which appeared to be identical with the usual "scattered reflections" continued to appear at virtual heights well above that of the last E multiple, and at frequencies near the previous value of f_{F2}, even though the reflections from F_2 had disappeared.

It is possible that these scattered reflections may be returned at frequencies considerably below f_{F2}, but the relatively great magnitude of the multiple reflections from the lower layers is likely to mask them completely. During the night, when f_{F2} is not well defined (see fig. 9) and complex reflections of large magnitudes occur above relatively low virtual heights, it is frequently difficult to determine when this effect begins to appear.

VII. SOME CORRELATIONS WITH RESULTS OF RADIO TRANSMISSION

It is of interest to observe that, using horizontal dipoles as transmitting and receiving aerials, directional toward each other, and over the 25-km land path between stations, the magnitude of the daytime reflections between a frequency somewhat below the E critical frequency and the F_2 critical frequency, ordinarily greatly exceeds the magnitude of the ground wave. The ratio of field intensities of the sky wave to those of the ground wave often exceeds 100:1. At night, the magnitude of the reflections becomes very much greater, particularly at the lower frequencies. The use of lower angle radiators, such as vertical antennas, of course, greatly reduces this ratio. Because of the effectiveness of the ionosphere as a reflector of waves of low frequency at night, the sky wave and ground wave may be of equal magnitude in an antenna only a very short distance from the transmitting station, even though only a very small amount of energy is radiated upward. This is particularly noticeable if the receiving antenna has a somewhat high-angle characteristic. The introduction of vertical antennas at the receiver serves to discriminate greatly against the high-angle sky-wave energy.

[57] Taylor and Young, Proc.I.R.E., vol. 16, p. 561, 1928; and vol. 17, p. 1491, 1929.

It is of interest to investigate the relation of the highest critical frequency of the F_2 layer at vertical incidence to the frequencies of waves received at great distances. The maximum frequency at which waves are reflected from the F_2 layer is very much less in summer than in winter. The values obtained are believed to be in fair agreement with the results obtained by a number of observers. Burrows [58] has pointed out that during 1928–1929 for trans-Atlantic transmissions, the highest summertime frequency at which waves could be transmitted across the Atlantic was 22,000 kc/s, while the highest wintertime frequency was 28,000 kc/s. The times of best trans-Atlantic high-frequency transmission shown in Burrows' figures for the various seasons correspond closely with the times of dip in the "virtual height contour maps" for the F_2 layer when consideration is given to the differences in time existing between the ends of the path.

This agreement might be expected in view of the F_2 layer results by which it was shown that the absorption was the lowest when the

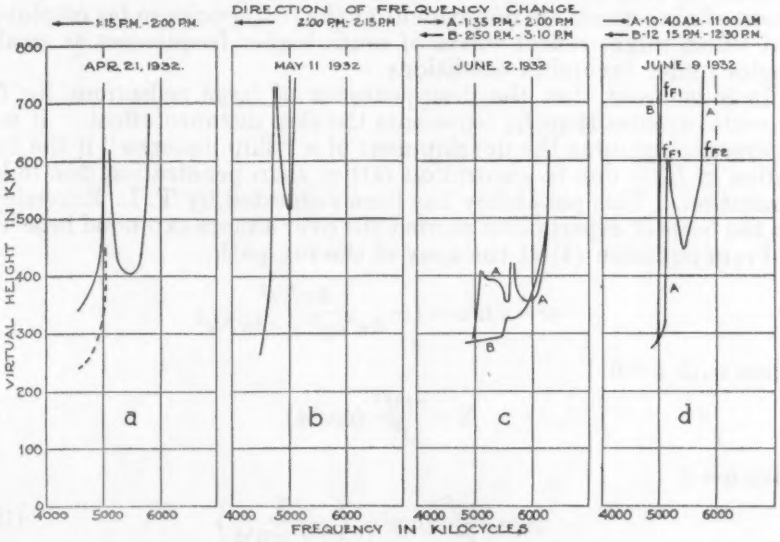

FIGURE 25.—*Examples of rapid changes in f_{F2}.*

frequency-height curves had the least slope, a condition occurring at the time of highest critical frequency. It can be seen that waves of the highest frequencies are returned over long paths when the highest (F_2) layer appears to be in the most favorable condition for reflection, and in general the diurnal and seasonal variations of such frequencies seem to follow changes in the condition of this layer. At the same time lower frequencies follow the somewhat different diurnal and seasonal variations of the lower layers.

In a previous section, the possibility that the disappearance of reflections might be due to absorption rather than to low ionization was discussed. Burrows suggests that the return of reflections at lower maximum frequencies during the summer than during the winter may be due to absorption. On the basis of this hypothesis, an ion density considerably in excess of that indicated by the maximum criti-

[58] Burrows, Proc.I.R.E., vol. 19, p. 1634.

cal frequency should be expected. It would be difficult to make even approximate estimates, however, because of the lack of data on the physical structure of the atmosphere in this layer. A suitable distribution of such high densities might account for the apparent occasional reflection from the ionosphere of waves at very high frequencies, such as have been frequently observed. It might be presumed that approximately north-south paths would be most uniform for such maximum-frequency transmissions. Such paths in the northern hemisphere would vary from a path running about north-northwest—south-southwest during winter noon to about north-northeast—south-southwest during summer evenings. Such paths extending between northern and southern hemispheres, however, would be subject to different seasonal effects as shown. More uniform conditions would probably exist during the afternoon. A detailed knowledge of these effects at different latitudes would make it possible to work out more definitely the conditions to be expected for various paths. It may also be possible that higher layers exist which on account of absorption are not evident at the frequencies so far employed, but which might reflect waves of much higher frequencies at smaller angles under favorable conditions.

It is believed that the disappearance of large reflections for frequencies greater than f_{F2} represents the skip distance effect. It is of interest to examine the development of a "skip distance" if the limitation of f_{F2} is due to absorption rather than penetration due to low ionization. This possibility has been suggested by T. L. Eckersley [59] on the basis of experiments carried out over a more extended base line.

From equation (4) at the apex of the ray path

$$n^2=\sin^2\phi=1-\frac{4\pi Ne^2}{4\pi^2mf^2+a4\pi Ne^2}$$

Then with $a=0$

$$N=\frac{\pi mf^2}{e^2}\ (\cos^2\phi) \tag{12}$$

with $a=\frac{1}{3}$

$$N=\frac{\pi mf^2}{e^2}\ (\cos^2\phi)\left(\frac{3}{2+\sin^2\phi}\right) \tag{12a}$$

This shows that for small angles of incidence (nearly vertical incidence) where $(\cos^2\phi)$ is nearly unity, the number of ions per cm^3 required to return reflections is not much reduced below that required at vertical incidence, and for boundaries of decreasing ionic gradient, the wave will be subject to the same high retardation and absorption observed at vertical incidence under these conditions. At the same time, the length of path subject to this increased absorption is extended horizontally as the angle of incidence, ϕ, is increased. When the value of ϕ becomes large enough to cause the factor $(\cos^2\phi)$ to depart appreciably from unity, the number of electrons per cm^3 required for refraction, and therefore the depth of penetration into the region of decreasing ionic gradient, decreases rapidly, and the length of path in which there is large absorption decreases. From this it might be expected that reflections at frequencies somewhat below f_{F2}, but pene-

[59] See footnote 51, p. 30.

trating deeply into the F_2 layer as determined by the curvature of the frequency-virtual height curves, may be subject to a considerable dip in intensity as the distance from the transmitter is increased, followed by an increase as the reflections are returned from a region of higher ionic gradient. It would also seem that absorption would prevent that portion of the layer represented by the steep slope of the frequency-height curves from returning reflections over any considerable distance. On this basis, it can be seen from the figures that a considerable variation in skip distance might be expected from day to day and from year to year. If this picture of the skip-distance phenomenon is correct, it may be expected that the portion of the F_2 layer represented by the steep slope of the frequency-virtual height curves will cause absorption of waves reaching this region.

WASHINGTON, August 23, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP633

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REACTIONS OF LITHOGRAPHIC PAPERS TO VARIATIONS IN HUMIDITY AND TEMPERATURE

By C. G. Weber and L. W. Snyder

ABSTRACT

In studies previously reported, information was obtained relative to causes of serious economic waste in offset lithography resulting from misregister in color printing. At the request of the Lithographic Technical Foundation, which is cooperating with the Bureau of Standards, further studies were made to obtain scientific data on the reactions of lithographic papers to variations in atmospheric humidity and temperature. Paper is a hygroscopic substance. Its moisture content is determined by the hygroscopic condition of the surrounding air, and its properties, particularly dimensional, are governed to considerable extent by moisture content. Since precise register requires constant dimensions, the influence of atmospheric changes was closely studied.

The dimensions of the papers varied directly with the miosture content regardless of the cause of the moisture changes. Moisture content was influenced by relative humidity, temperature, and history of conditioning Humidity changes were most important. A 10-point change affected the moisture content sufficiently to alter the dimensions enough to cause serious misregister. Temperature effects were less important, but of sufficient magnitude to call for close control in printing. History of conditioning had an important influence on equilibrium moisture content, hence on dimensions.

The paper that gave best register in printing had the lowest coefficient of expansion in the machine direction, and the paper that gave the largest misregister had the highest. The papers with low expansion in the machine direction have correspondingly high expansion in the cross direction, which indicates the desirability of large directional difference in fiber formation of offset papers. The low coefficient of expansion in machine direction for the papers giving best register, indicated that distortion in printing which affects register is caused largely by moisture content variations.

The usual sizing materials had little influence on the moisture content response of paper to changing relative humidity except with respect to the rate of change. Both surface sizing and mineral coatings increased the total dimensional changes per unit of moisture content change. The effects of ordinary atmospheric changes on strength properties were not of sufficient magnitude to be of significance in lithography.

CONTENTS

	Page
I. Introduction	54
II. Description of papers and method of study	54
III. Results of studies of the paper reactions	58
1. Rate of conditioning	58
2. Influence of relative humidity on strength properties	58
3. Temperature and moisture content	58
4. Relative humidity and moisture content	59
5. Influence of moisture content on dimensions	62
IV. Recommendations	64

I. INTRODUCTION

Results obtained in studies of register in offset printing made at the Bureau of Standards in cooperation with the Lithographic Technical Foundation, and reported in a previous article,[1] made apparent the need of more exact data relative to the behavior of paper with changing atmospheric conditions. The avidity of paper for moisture, and the fact that its properties and dimensions vary with its hygroscopic state, have long been known, and numerous articles [2] containing information on the subject may be found in the literature. However, practically no information was available on the exact physical behavior of large sheets of paper when exposed to atmosphere at variance with the hygroscopic state of the paper; the influence of initial moisture content on conditioning; the exact relation of moisture content to dimensions; the separate effects of temperature and relative humidity; or the importance of small atmospheric changes. In order to obtain such information, specially prepared papers of known history, and known response to the offset-printing process, were studied at various humidites and temperatures. Success in offset printing cannot be attained if paper changes in dimensions to any appreciable extent during the interval between printing the first and last colors. Since the moisture content of paper is determined by the surrounding air and all changes are accompanied by dimensional changes, particular attention was given to the influence of humidity and temperature on the moisture content, and to the resulting dimensional changes. In considering the test results, it should be remembered that both the rate and the extent of reactions of paper caused by changes in atmospheric moisture and temperature, are influenced by components of paper and its physical characteristics. Comparatively soft porous papers, such as the lithographic papers, would absorb moisture more rapidly and with less change in their dimensions than harder and denser paper, such as bond.

II. DESCRIPTION OF PAPERS AND METHODS OF STUDY

The papers studied were those used in the register experiments reported in Bureau of Standards Research Paper No. 480, and have the same identification numbers. In addition, two rosin-wax sized papers, made in the Bureau's experimental mill, were included. Test data for the papers studied and a description of the papers are contained in table 1.

[1] Weber, and Cobb, B.S. Jour. Research, vol. 9, p. 427 to 440, September 1932.

[2] Griffin, Paper Trade Jour. 85, TS 43, 1927. Houston, Carson, and Kirkwood; Paper Trade Jour. 76, no. 15, p. 237, April 12, 1923. Jarrell, Paper Trade Jour. 85, TS 23, 1927. Kiely, Paper Trade Jour., 80, no. 6, p. 207, Feb. 5, 1925. Kress and McNaughton, Paper, 22, no. 24, p. 11, Aug. 21, 1918. Kress and Silverstein, Paper, 19, no. 25, p. 13, Feb. 28, 1917. Reed, Handbook of air conditioning for lithographers, Lithographic Tech. Found. Carson, Paper Trade Jour. 93, no. 18, p. 71 to 74. Oct. 29, 1931. Carson and Worthington, Paper Trade Jour., 94, no. 2, p. 34 to 42, Jan. 14, 1932. McKee and Shotwell, Paper Trade Jour., 94, no. 22, p. 33 to 37, June 21, 1932. McKee and Shotwell, Paper Trade Jour., 97, no. 6, p. 33 to 42, Aug. 10, 1933.

TABLE 1.—*Test data of the papers studied*

Sample number	Weight, 25 by 40 inches, 500 sheets	Thickness	Bursting strength	Folding endurance [2]		Tensile properties [3]				Water resistance—dry-indicator method	Ash	Opacity	Description
				Machine direction	Cross direction	Breaking load		Elongation at rupture					
						Machine	Cross	Machine	Cross				
	Pounds	*Inch*	*Points* [1]	*Double folds*	*Double folds*	*Kg*	*Kg*	*Percent*	*Percent*	*Seconds*	*Percent*	*Percent*	
1	78.1	0.0049	24.3	52	15	6.9	3.3	1.5	3.2	53.7	9.9	96.2	Machine-finish litho, light beating, light jordanning.
2	74.3	.0042	21.1	18	11	5.5	3.0	1.6	3.7	31.9	11.7	96.2	Machine-finish litho, light beating, heavy jordanning.
3	73.8	.0044	21.4	25	10	5.9	3.0	1.1	2.6	44.1	9.9	95.2	Machine-finish litho, normal beating, light jordanning.
4	69.2	.0040	20.7	14	11	5.2	2.9	1.3	3.9	31.5	11.5	94.4	Machine-finish litho, normal beating, heavy jordanning.
5	79.8	.0048	33.0	62	29	8.5	4.1	1.7	3.7	48.4	9.5	95.2	Number 1 surface sized with starch.
6	82.0	.0049	25.9	12	15	7.6	3.9	1.5	3.8	63.3	12.1	96.1	Number 2 surface sized with starch.
7	77.7	.0047	27.9	46	17	8.0	3.8	1.3	3.7	43.4	9.1	94.4	Number 3 surface sized with starch.
8	76.6	.0047	25.1	14	10	7.1	3.8	1.5	4.2	55.3	10.5	95.6	Number 4 surface sized with starch.
9	70.2	.0032	21.7	55	10	5.5	2.6	2.3	3.1	19.1	35.7	95.1	Coated litho, no sizing in raw stock.
11	76.2	.0037	21.2	38	12	5.4	2.6	2.1	3.4	26.3	35.2	96.4	Coated litho, normal sizing in raw stock.
13	56.3	.0033	20.0	28	12	5.9	2.8	1.5	3.3	12.1	7.2	87.7	Extra strong machine-finish litho with no sizing.
14	54.4	.0034	19.6	24	10	5.5	2.5	1.6	3.4	19.3	8.0	88.4	Extra strong machine-finish litho with one half normal sizing.
16	56.9	.0036	27.0	160	230	7.1	4.4	2.0	5.5	35.2	--------	83.3	Bond type paper, sized with rosin-wax size.
17	55.6	.0037	27.0	140	240	7.8	4.3	1.5	5.5	27.9	--------	80.7	Bond type paper, sized with rosin-wax size.

[1] Bursting pressure in pounds per square inch through a circular orifice 1.2 inches in diameter.
[2] For test specimen 15 mm wide and 90 mm between jaws.
[3] For test specimen 15 mm wide and 100 mm between jaws.

The studies were made in a room of approximately 1,080 cu.ft. in which humidity and temperature were controlled by means of a humidifying-dehumidifying unit, capable of conditioning air at the rate of 2,500 cu.ft. per minute, thus providing a change of air every 30 sec. Great care was exercised in measuring the humidity. A continuous record was kept by means of a hygrothermograph which was checked at frequent intervals with an aspiration-type psychrometer equipped with sensitive calibrated thermometers, motor driven suction fan, reading glass, and wick feed for wet bulb.[3] The papers

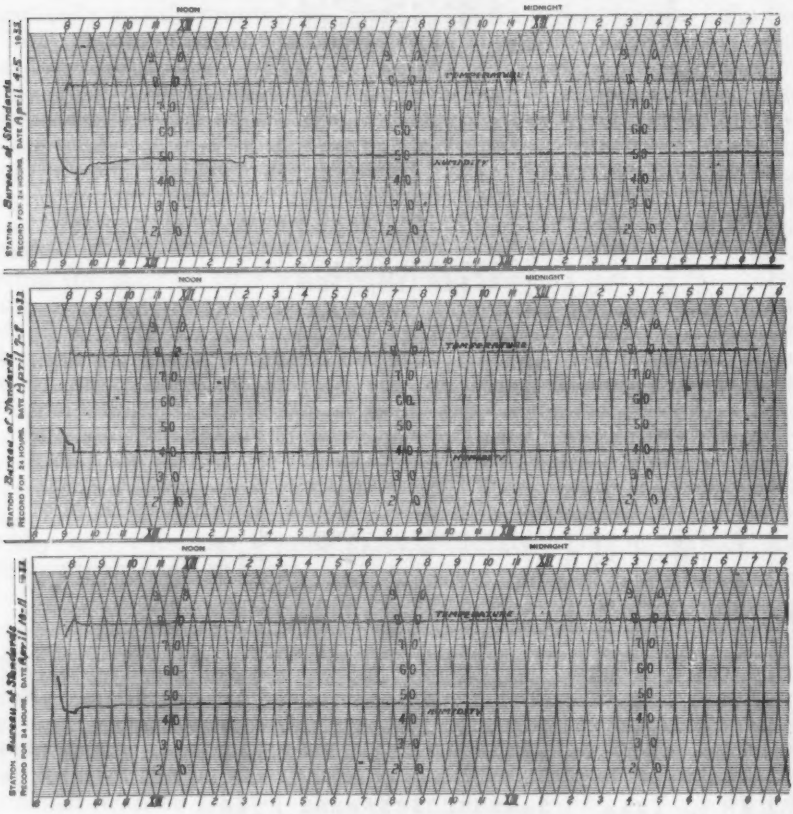

FIGURE 1.—*Three typical temperature humidity records.*

were conditioned at approximately 5 ft. above the floor and were tested on a bench about 2 ft. below the space in which they were conditioned. In conditioning the specimens, they were hung from their corners so as to expose both sides of every sheet. The humidity was controlled to within ±0.5 percent and the temperature to within ±0.5° F. The typical hygrothermograph records reproduced in figure 1 illustrate the control maintained.

The reactions of the papers were determined by conditioning test specimens until hygroscopic equilibrium was reached, and then measuring the changes in their properties. The specimens were kept in

[3] Carson and Worthington, Paper Trade Jour. 94, no. 2, p. 34 to 42, Jan. 14, 1932.

sealed containers while humidity or temperature changes were being made in the room. Dimensional measurements were made accurately to 0.002 of an inch on specimens 24 by 24 inches, by means of a micrometer rule.[4] Separate specimens, weighing approximately 15 grams each, were used for moisture determinations. Their weights were determined accurately to 0.1 mg, at each atmospheric condi-

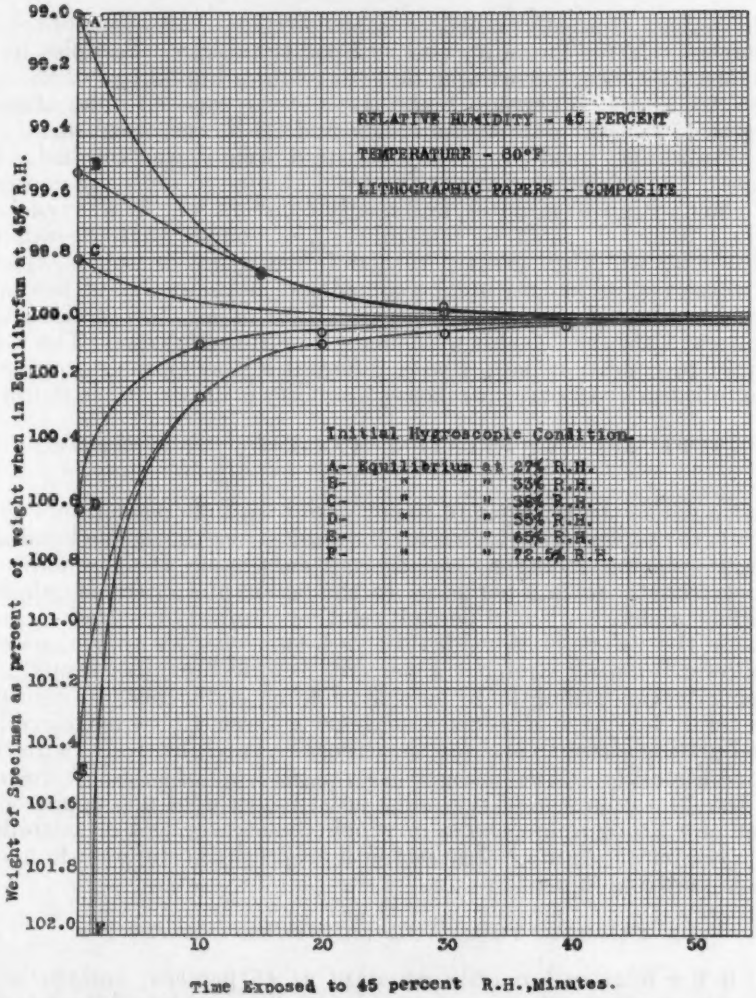

FIGURE 2.—*Rate of conditioning for papers with different moisture contents.*

tion, and their moisture contents were computed from the oven dry weights obtained at the conclusion of experiments. All samples were exposed 18 to 20 hours, although, in all cases, the weights of the specimens were practically constant in less than one third of that time. The precision with which the work was done is illustrated by the regularity of the curves shown later in the article. Numerous

[4] Weber and Cobb, B.S. Jour. Research, vol. 9, p. 431, September 1932.

check tests were made with respect to moisture content determinations, and in these tests the average variations from the original values was less than 0.1 percent.

III. RESULTS OF STUDIES OF THE PAPER REACTIONS

1. RATE OF CONDITIONING

The papers studied reached constant weight in an atmosphere of 45 percent relative humidity and 80 F quite rapidly. Samples having moisture contents corresponding to relative humidities of 28, 33, 38, 55, 65, and 72.5 percent, respectively, were exposed in an atmosphere of 45 percent relative humidity and 80 F, and weighed at 10-minute intervals until practically constant weight was reached. In all cases, 75 percent or more of the total change in moisture content took place within 10 minutes, and nearly constant weight was reached within 1 hour. It must be remembered, of course, that the rate of conditioning will vary greatly with different types of papers, therefore, these results should not be considered as indicative of the rate of conditioning of papers in general. Rate of air flow around the samples will also be a factor influencing conditioning time. The time required to condition papers with different initial moisture contents to equilibrium at 45 percent relative humidity is illustrated in figure 2.

2. INFLUENCE OF RELATIVE HUMIDITY ON STRENGTH PROPERTIES

Inasmuch as the strength of paper varies with changes in moisture content, the papers were tested for bursting strength, tensile breaking strength, tearing strength, and folding endurance at 7 humidities, ranging from 27 to 72.5 percent. In the region of 45 percent relative humidity, a change of ± 10 percent relative humidity resulted in variations in the values obtained for the various properties approximately as follows: Bursting strength, 1 percent; tensile breaking strength, 5 percent; tearing strength, 10 percent; folding endurance, 10 percent. In general, folding endurance and tearing strength varied directly, while bursting strength and tensile strength varied inversely, with the relative humidity. The changes in strength were of such low magnitude that the influence of humidity on strength does not appear significant for lithographic plants in which the atmosphere is controlled within reasonable limits. The strength properties at different humidities are shown in figure 3.

3. TEMPERATURE AND MOISTURE CONTENT

With the relative humidity constant at 45 percent, variations in temperature within the range 69 to 110 F were found to have a well-defined and regular influence on moisture content. Over the range studied, the average moisture content varied inversely with the temperature. The percentage of moisture content varied at the rate of 0.15 per 10 F change in temperature. A temperature effect of such magnitude makes temperature control to within ± 5 F appear essential in plants having conditioned air, if the full benefits of humidity control are to be obtained. It also indicates the importance of close control of temperature in the physical testing of paper. The relation of temperature to moisture content is illustrated in figure 4.

4. RELATIVE HUMIDITY AND MOISTURE CONTENT

Paper reacts to a change in the relative humidity of the surrounding air by a readjustment of moisture content, and changes in its properties result. Although many investigators have studied the effects of

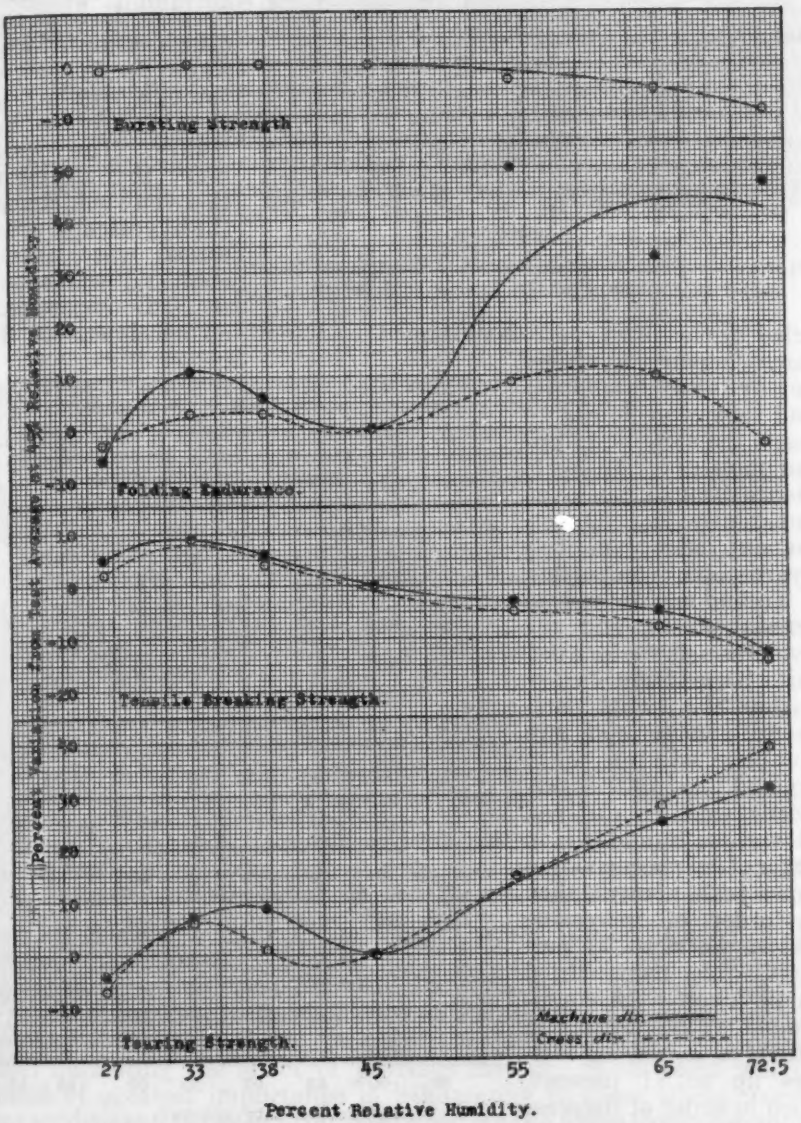

FIGURE 3.—*The influence of variations in relative humidity on strength properties of lithographic papers with constant temperature, 80 F Composite —13 lithographic papers.*

humidity on the moisture content of paper and other fibrous materials, no complete data were available to indicate exactly how the history of the hygroscopic state of paper determines its equilibrium condition

for the range of conditions commonly encountered. Hence the hysteresis effects of adsorption and desorption of moisture on equilibrium moisture content were studied. The range studied was 34 to 71 percent relative humidity at 80° F. temperature. Specimens dried in the oven and others saturated over water were taken through regular cycles of relative humidity. The possibility that drying in the oven would change the hygroscopic properties was considered and the effects studied. Specimens dried in the oven were conditioned with undried specimens of the same paper at widely separated humidities and they were found to reach the same equilibrium moisture content. Hence drying in the oven apparently had no permanent effect on the hygroscopic properties.

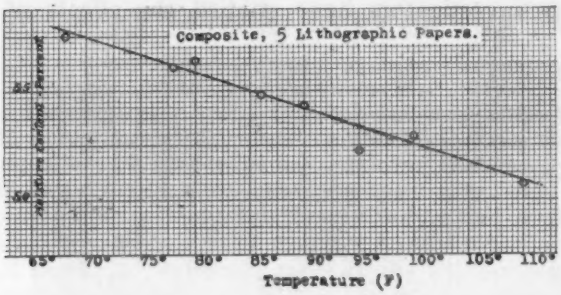

FIGURE 4.—*Relation of temperature to moisture content of paper with constant relative humidity 45 percent.*

To find maximum hysteresis effects, and the hysteresis effects for a definite humidity range within the limits commonly encountered, two complete cycles were studied. Saturated specimens were conditioned at various humidities in order of decreasing values down to 34 percent, then in order of increasing values back to 71 percent. Specimens dried in the oven were conditioned at humidities in order of increasing values up to 71 percent, then in order of decreasing values back to 34 percent relative humidity. In figure 5 the resulting changes in moisture content equilibrium are shown graphically. The curve showing moisture loss for the saturated specimens and that showing moisture gain for the oven-dry samples apparently represent,

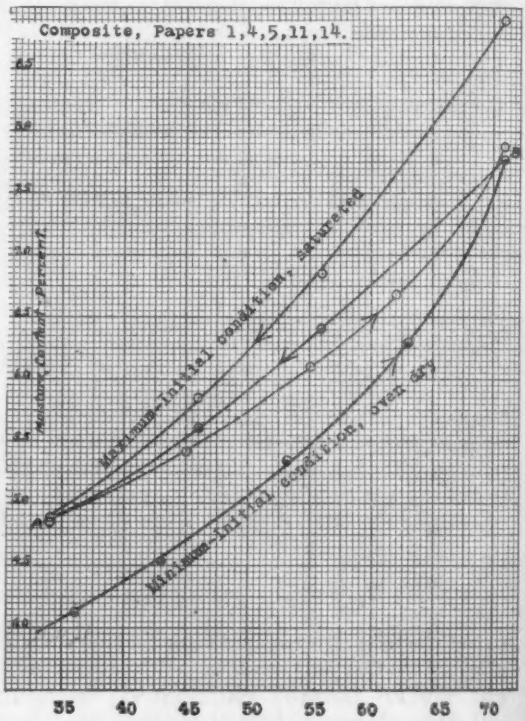

FIGURE 5.—*Equilibrium moisture content of papers at different relative humidities.*

respectively, maximum and minimum moisture content values for these papers within the ordinary humidity range. Therefore the distance between the maximum and minimum curves at any point indicates the maximum hysteresis effect at that humidity.

It will be noted that the specimens with maximum and minimum moisture equilibriums at 71 percent humidity reached the same equilibrium moisture content after conditioning downward to 34 percent to *A*. Likewise, the specimens with maximum and minimum at the low humidity, 34 percent, reached identical equilibrium states after conditioning upward through a humidity range of 36 percent to *B*. From a consideration of this behavior, it appears that the region inclosed between the curves joining *A* and *B* represents the maximum hysteresis range for papers conditioned within the range of 34 to 71

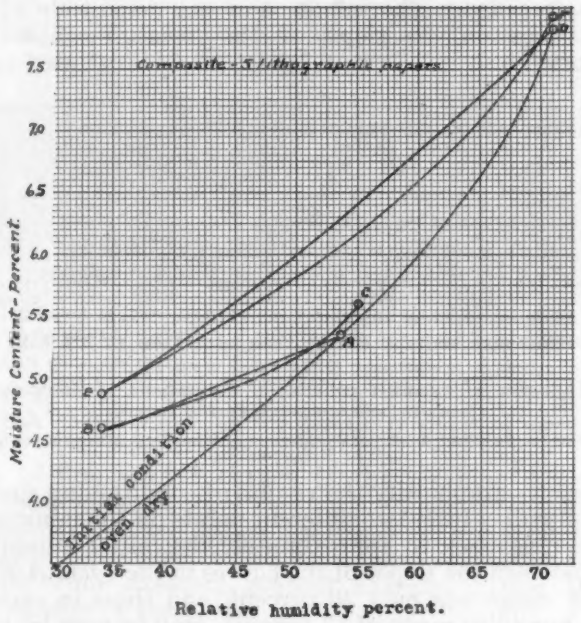

FIGURE 6.—*Influence of magnitude of humidity changes on slope of moisture-content, relative-humidity curves, and hysteresis effects.*

percent relative humidity, provided they are preconditioned at 34 percent for adsorption or at 71 percent for desorption. The small hysteresis range for these particular conditions in contrast with the large hysteresis range for the extreme conditions of preconditioning, emphasize the desirability of a definite conditioning procedure rather than neglecting the effect of previous history. This point will be found of greatest importance in lithography in cases where papers are conditioned between printings to restore the hygroscopic condition to that at the first printing, or in precise testing where paper is conditioned for the purpose of obtaining a standard hygroscopic condition. Separating *A* and *B* on the humidity scale should increase the hysteresis range. Bringing them closer together should decrease it. The range of 34 to 71 percent relative humidity, which represents the extremes conveniently obtained with good control apparatus, covers ordinary practice without excessive hysteresis.

The effects of small humidity changes on moisture content, and the influence of the magnitude of the total equilibrium change on hysteresis, were studied. Oven-dry specimens were conditioned first at 40 percent R.H. and then at 48, 40, 45, 40, 42.5, 40, 37, 40, 35, and 40 percent, in that order, and the moisture content determined for each condition. The slope of the curve for relative humidity and moisture content was found to depend on the magnitude of the total humidity change. Increasing the total change increased the moisture content change per unit of humidity change until the limit as represented by the maximum and minimum moisture content curves was reached. Also, the magnitude of the hysteresis effect depended upon the total humidity change involved; it increased with increase in the total humidity change until the maximum hysteresis, shown as the distance between the maximum and minimum moisture content curves in figure 5, was reached. The influence of the magnitude of the total humidity change on the slope of the moisture-content relative-humidity curve, also its effect on hysteresis, is illustrated in figure 6.

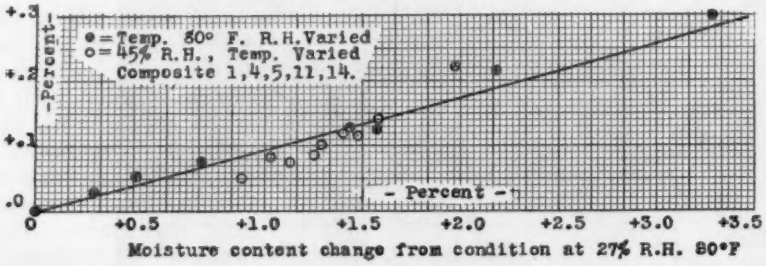

FIGURE 7.—*Influence of moisture content on dimensions of lithographic papers, variations in both temperature and humidity.*

The percentage values at the left are dimensional changes as variation from dimensions at 27 percent R.H. and 80° F. temperature,

This chart shows graphically the results of conditioning specimens to 34 percent humidity from two different points on the minimum curve, then conditioning back to approximately the initial humidity. The differences between the slopes of the curves in the cycle *A-B-C*, where the humidity range was only 20 percent, and those in cycle *D-E-F*, with a total humidity range of 37 percent, may be seen by comparing curve *A-B* with *D-E*, and *B-C* with *E-F*.

5. INFLUENCE OF MOISTURE CONTENT ON DIMENSIONS

The dimensions of paper are influenced by its hygroscopic moisture through a swelling of the individual fibers. The data obtained in this study indicate that, within the range of atmospheric conditions ordinarily encountered, the dimensions vary directly with the moisture content irrespective of the cause of the moisture change. Figure 7 illustrates the influence of the hygroscopic state on the dimensions of lithographic papers. The values used are averages for papers 1, 4, 5, 11, and 14 which represent the different types of lithographic papers studied. It will be noted that the data obtained for different humidities with constant temperature, and for different temperatures with constant humidity, result in a single regular curve.

Of papers 1, 2, 3, and 4, which differed only with respect to degree of mechanical treatment of fibers in manufacture, no. 1, which was

prepared with the minimum of beating [5] and jordanning,[6] changed least in the machine direction of the paper (the direction parallel to the forward movement of the paper machine), or, as it is often termed, "with the grain", with variations in moisture content. In figure 8 the dimensional changes of paper no. 1 are shown in comparison with the average for the group comprising papers, 1, 2, 3, and 4. These results corroborate the evidence obtained in the printing tests [7] that paper prepared with the minimum of beating and jordanning is best suited to multi-color offset printing because it changes

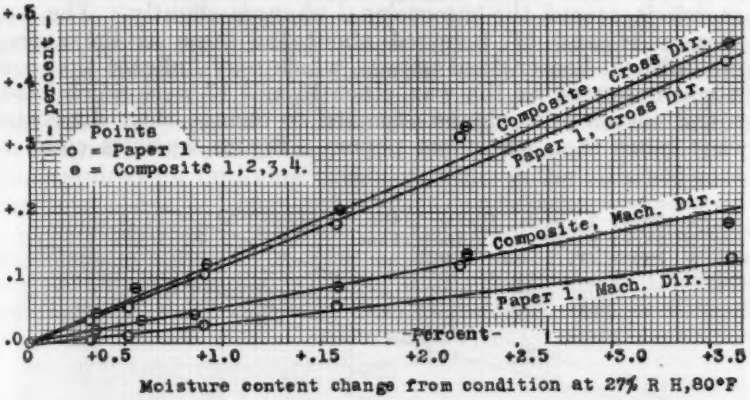

FIGURE 8.—*Influence of moisture-content variations on dimensions of lithographic papers. Comparison of paper no. 1 with the average of no. 1, no. 2, no. 3, no. 4.*

Values at the left are dimension changes as variation from dimensions at 27 percent R.H. and 80 F. temperature.

least along the "back edge", as the printer terms it (a machine direction change), in successive printings. Since the paper having the lowest rate of dimensional change in the machine direction with moisture content changes, gave best register, and the paper with the highest rate of change gave the poorest register of prints,[8] it is apparent that the paper distortions which most seriously affect register of prints, result from moisture content changes, rather than from mechanical stresses of the press.

It is particularly significant to note in connection with the moisture-content dimensional relationship illustrated in figure 5, that the large directional difference with respect to expansion in the case of paper 1 is indicated by the physical strength values shown in table 1. In folding endurance, the ratio of the machine direction strength to the cross direction strength, is about 3.5 to 1 for paper 1 as compared to 2 to 1 for the average of papers 1, 2, 3, and 4. This is to be expected since large directional difference in strength indicates that a relatively large percentage of the fibers are parallel to the machine direction. Since the dimensional change of an individual fiber with adsorption

[5] Beating is the term applied to the mechanical treatment given to papermaking materials, suspended in water, to prepare them for forming a sheet on the paper machine. Beating separates, brushes, and frays-out the fibers, and causes them to absorb water.

[6] Jordanning is a refining process that usually follows beating to complete the preparation of the materials for forming a paper of the desired character. In the jordan the fibers are freed from lumps and cut to the desired length.

[7] Weber and Cobb, B.S. Jour. Research, vol. 9, pp. 437 to 438, September 1932.

[8] Register Studies in Offset Lithography, B.S. Jour. Research, vol. 9, pp. 437 to 439, September 1932.

or desorption of moisture is largely a diameter change, the paper having the greatest number of fibers parallel to the machine direction will have the lowest dimensional change in that direction, and a correspondingly large change in the cross direction, as this direction is parallel to the diameter of the largest number of fibers. Hence it appears that large directional difference in strength properties of paper is an indication of good sheet formation for offset printing.

Of the different types of paper studied, the coated paper had the largest dimensional change per unit of moisture content variation, and the machine finished offset papers had the lowest. Surface sizing with starch increased the dimensional changes slightly. The wax-sized papers 16 and 17, behaved about the same as the average machine-finished, beater-sized papers, which may indicate that some benefit was imparted by the wax, since 16 and 17 were much harder papers and therefore would be expected to change their dimensions somewhat more than the offset papers. Figure 9 shows compara-

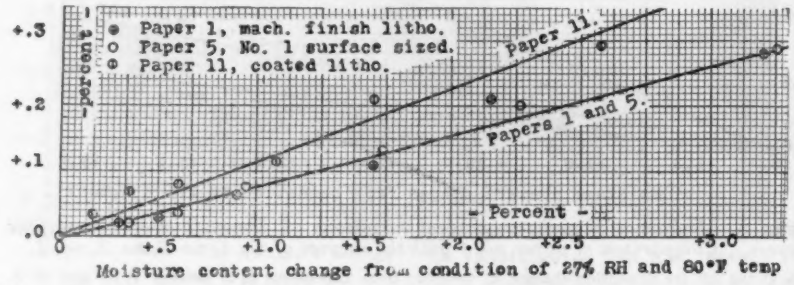

FIGURE 9.—*Influence of moisture content on dimensions of lithographic papers Comparison of machine finished, surface sized, and coated papers.*

Values at the left are dimension changes as variation from dimensions at 27 percent R.H. and 80 F. temperature.

tively the relation of the moisture content to dimensions of machine finished lithographic paper 1, paper 5, which is paper 1 surface sized with starch, and paper 11, a coated paper.

IV. RECOMMENDATIONS

From a consideration of the influence of humidity and temperature on the moisture content of the papers, it is obvious that precise register in lithography requires atmospheric control within narrow limits. The relative humidity should be controlled to ± 2.5 percent and temperature to $\pm 5°$ F. Air-conditioning apparatus for lithographic plants should be designed to control within those limits.

The hysteresis effects of adsorption and desorption of moisture were found to be important. In precise testing, where paper is conditioned to obtain a standard hygroscopic condition for a given relative humidity, or in printing where the paper is reconditioned between printings to restore the hygroscopic condition to that at first printing, a definite conditioning procedure should be established and followed.

Sheet formation of paper was found extremely important with respect to machine direction distortion with hygroscopic changes. Paper for multicolor offset printing should be made with an absolute minimum of beating and jordanning of fibers, and should be

so formed as to obtain the greatest possible directional difference by having the length of the greatest possible number of fibers parallel to the machine direction.

Surface sizing and surface coating of paper increased somewhat the distortion with hygroscopic changes. Hence, for most precise register of prints, machine-finish papers are recommended.

Tests of lithographic papers should include the folding endurance test as the directional difference is reflected sharply in the folding endurance.

Additional definite recommendations must await further printing plant studies. Determination of the influence on register in printing exerted by the conditioning factors already found important, development of information on commercial scale paper conditioning, and further fundamental study of the relation of fiber properties to distortion of paper in printing are planned for future study. The development of specifications that will adequately define the properties required for optimum printing results is the ultimate goal in this work.

Acknowledgment is made of the invaluable assistance of the advisory committee of the Lithographic Technical Foundation under the chairmanship of Prof. R. F. Reed, also of the advice and assistance of B. W. Scribner, chief of the paper section of the Bureau of Standards, and F. T. Carson, and R. W. Carr of the paper section.

WASHINGTON, October 11, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP634

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A GLASS ELECTRODE POTENTIOMETER SYSTEM FOR THE DETERMINATION OF THE pH VALUES OF WEAKLY BUFFERED SOLUTIONS SUCH AS NATURAL AND TREATED WATERS [1]

By John O. Burton, Harry Matheson, and S. F. Acree

ABSTRACT

In the electrometric measurement of the pH values of buffered solutions more dilute than $M/10{,}000$ by means of quinhydrone and hydrogen electrodes the resistance of the solution, escape of carbon dioxide, acid properties of the quinhydrone, and polarization of the electrodes are so disturbing that the emf readings may vary as much as 5 to 30 mv or 0.1 to 0.5 pH unit. The isohydric-indicator technique is apparently applicable within 0.1 pH to such solutions, and distilled water, but has not heretofore been compared with a reliable emf method. By adding Varley shunts to a modification of the vacuum-tube potentiometer used by Partridge, keeping the grid attached to the circuit, and using a Thompson glass electrode, emf readings can be made within 0.1 to 2.0 mv on weakly-buffered solutions and distilled water, and the pH values agree with those obtained by the isohydric-indicator method. This apparatus is also suitable for measuring the pH of solutions containing active oxidizing or reducing agents, such as chlorine or tannins, where the hydrogen and quinhydrone electrodes and indicator methods might fail.

CONTENTS

		Page
I.	Introduction	67
II.	The glass electrode potentiometer system	68
III.	The pH measurements	71
IV.	Summary	72

I. INTRODUCTION

The methods most frequently used for determining hydrogen-ion concentrations include the hydrogen electrode, the quinhydrone electrode, and indicators. All have their limitations, either as to the range of concentration in which they are applicable or to the type of solutions in which they can be used. For example, oxidizing agents such as chromates and chlorine interfere. The glass electrode, on the other hand, has been shown [2] by Hughes, MacInnes, Thompson, and others to be applicable in solutions of oxidizing and reducing agents, and of heavy metal salts, when the pH values are less than 11 or 11.5. There are no data showing the lowest concentrations in which the glass electrode is applicable.

[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the Eighty-Fifth Meeting of the American Chemical Society, Washington, D.C., Mar. 27 to 31, 1933.

[2] For extensive references see M. R. Thompson, B.S.Jour. Research, vol. 9, p. 852, 1932.

In connection with our work on the determination of the pH and total acidity of the weakly-buffered extracts of paper and farm-waste fibers and of sugar acids in equilibrium with their lactones and salts, it became necessary to devise a method applicable to both the solutions and the natural and distilled water used as solvents. It was found by Fawcett and Acree,[3] and confirmed by ourselves, that the hydrogen electrode is not very sensitive in solutions more dilute than $N/10{,}000$, due to the high resistance and polarization at the electrode; in such cases the readings with portable galvanometers are not reliable within several tenths of a pH unit. Furthermore the pH will rise steadily as the hydrogen removes carbon dioxide from the solution. In the use of the quinhydrone electrode the quinhydrone itself, as an acid, lowers the pH steadily as it gradually dissolves and the error is consequently large, in some cases several tenths of a pH unit, with very dilute buffers such as natural and distilled waters. On the other hand the above authors have shown that consistent pH readings can be obtained on dilute buffers or distilled water by the isohydric-indicator method, in which a final check is made by adding indicator adjusted to the pH of the unknown as determined in preliminary tests. As the high resistance of dilute solutions or even pure water in the usual glass-electrode vessels is small in comparison with that of the glass itself, which is generally greater than 10 megohms, this emf method looked promising. It has proven useful within its range in this field for giving a very desirable comparison between the pH values obtained by its use and by the isohydric-indicator technique. The method is particularly promising for measuring the hydrogen-ion activity of organic acids and acid salts (buffers) and applying the mass law in extremely dilute solutions that approach pure water.

Check readings with the glass electrode on even double-distilled water do not vary more than 2 to 3 mv which is satisfactory for most purposes. Although only meager data are available, the results of Thompson [4] are supported regarding the salt errors of the glass electrode, which gives approximately the same pH as the isohydric-indicator technique below pH 7.0. The object of this paper is therefore to present data obtained by these four methods in very dilute or weakly-buffered solutions and distilled water, and particularly to show the usefulness and agreement of the glass electrode and the isohydric-indicator methods, and the sources of error of the hydrogen and quinhydrone electrodes.

II. THE GLASS ELECTRODE POTENTIOMETER SYSTEM

The equipment consists essentially of a Leeds and Northrup type K potentiometer and type R 500 ohm 2500-e galvanometer, sensitive to 0.01 mv per mm and with a period of 3 seconds, a Thompson metal-jacketed electrode and saturated calomel electrode, and a modified Partridge [5] vacuum-tube galvanometer containing a special Duovac triode requiring 2 volts for the filament and -1.5 volts on the grid. The authors' more recent work is being done with the FP 54 G.E. tube, which is even more suitable for the purpose. Figure 1 illustrates in the upper sketch the approximate values of the resistances and the

[3] Edna H. Fawcett and S. F. Acree, Jour. Bacteriology, vol. 17, no. 3, March 1929; Jour. Ind. Eng. Chem. An. Ed., vol. 2, p. 78, Jan. 15, 1930.
[4] See reference 2, p. 67.
[5] H. M. Partridge, Jour. Am. Chem. Soc. 51, 1, 1929, Microchemie, 11, 326, 337, 1932.

changes made in the Partridge system which is shown in the lower diagram. The letters show the positions of the switches in the Partridge instrument. In following the directions furnished for the Partridge apparatus the A and B batteries are turned on and reach fairly stable conditions in about 30 minutes as shown by the milliammeter. The grid circuit is left open, and the galvanometer deflection is brought to zero by sliding its movable contact terminal along the B battery negative line. The grid-circuit contact is then closed and moved

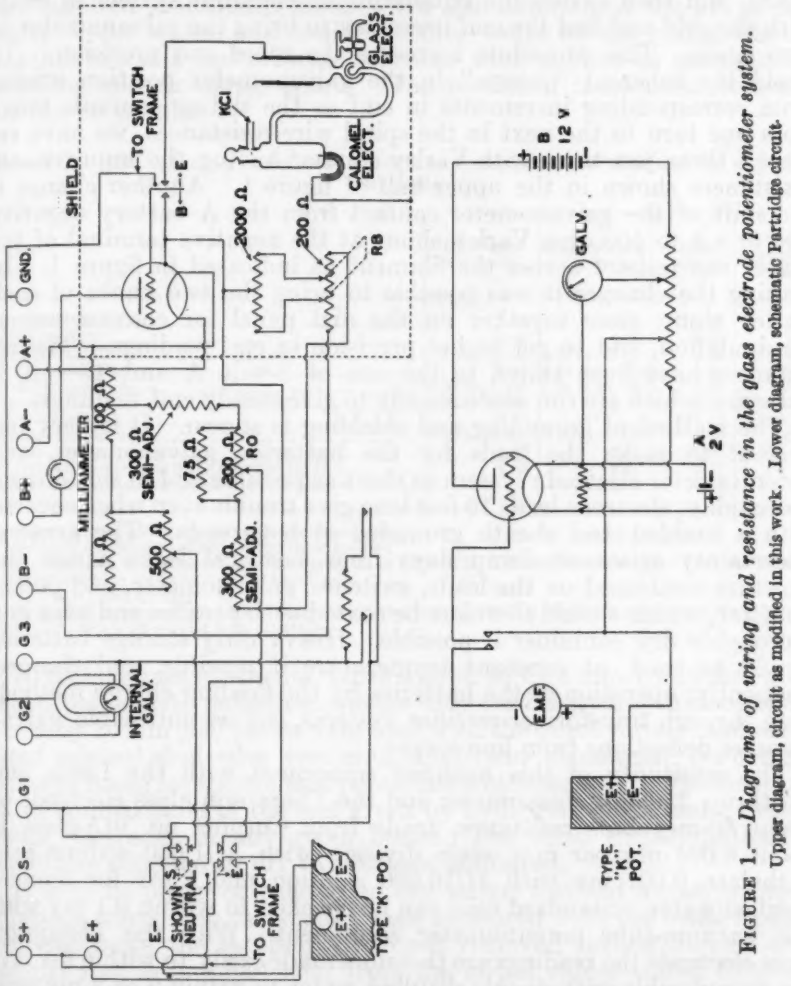

FIGURE 1.—*Diagrams of wiring and resistance in the glass electrode potentiometer system.*
Upper diagram, circuit as modified in this work. Lower diagram, schematic Partridge circuit.

along the B battery negative line to balance the galvanometer again. These operations are repeated until the galvanometer deflection is zero regardless of whether the grid circuit is closed or open. The electrode system and potentiometer are then switched into series with the grid, and the emf of the electrode system is found by adjusting the potentiometer until the galvanometer reading is again zero. All this manipulation takes time for readings to 0.1 mv and is rendered difficult by the disturbing effect of stray charges on the free grid po-

tential which good shielding cannot completely overcome around heavy-current equipment.

We have noted that the balances are more easily obtained with the grid circuit closed because they are then less affected by stray electrical impulses. All balancing with a free grid is therefore omitted. Simply contact the grid lead with the B battery negative line at approximately the correct position, adjust the movable galvanometer terminal on the B battery negative line until zero reading is established, and then switch the potentiometer-electrode system in series with the grid and find the emf necessary to bring the galvanometer to zero again. This procedure increases the speed and precision. To avoid the inherent "jumps" in the galvanometer position arising from corresponding increments in emf as the sliding contacts move from one turn to the next in the spiral wire-resistances, we have replaced these junctions with Varley shunts[6] having the approximate resistances shown in the upper half of figure 1. Another change is the shift of the galvanometer contact from the A battery negative line to a 1 to 500 ohm Varley shunt at the negative terminal of the center tap resistor across the filament as indicated in figure 1. In making the changes it was possible to bring the two knobs of each Varley shunt close together on the dial panel for convenience of manipulation, and to get higher precision in emf readings. The resistances have been suited to the use of 2-volt A and 12-volt B batteries, which are run continuously to give steady emf readings.

The method of grounding and shielding is shown. It is very important to make the leads for the batteries, galvanometer, and potentiometer-electrode system as short as possible and to shield them thoroughly; electrode leads 10 feet long give trouble even when covered with a braided-steel sheath grounded at both ends. The greatest uncertainty arises on damp days from electrical leaks across the moisture condensed on the leads, switches, galvanometer, and potentiometer, which should therefore be coated with paraffin and kept in a thoroughly dry container if possible. Heavy duty storage batteries should be used, at constant temperature if possible, and charged frequently; operation of the batteries by the floating charge method, even through transformer-rectifier systems, causes noticeable galvanometer deflections from line surges.

The sensitivity of this modified equipment with the Leeds and Northrup 2500-e galvanometer and the Thompson glass electrode of about 60-megohms resistance, made from Corning no. 015 glass, is about 0.004 mv per mm scale division with $M/1{,}000$ sodium-acid phthalate, 0.007 mv with $M/10{,}000$ solution, and 1 mv for double-distilled water. Standard cells can be checked to within 0.1 mv with this vacuum-tube potentiometer equipment. With the Thompson glass electrode the readings are therefore made easily to within 0.1 mv, are reproducible with double-distilled water to within 2 or 3 mv, and become better as the buffer concentration increases.

[6] The Varley shunt was made by arranging an ordinary radio potentiometer with two insulated sliding contacts close together, and shunting them with another potentiometer. A knob on the main potentiometer gives the coarse adjustment and the knob on the shunt potentiometer gives very fine adjustments in emf.

III. THE pH MEASUREMENTS

The purpose of this work was to learn the limiting dilutions of organic buffer salts in which each of the methods mentioned can be used and to get similar data on natural, treated, and distilled waters generally used as solvents. We therefore first used each of the four methods to measure the pH of solutions of sodium-acid phthalate (NaHPh in the tables) whose concentrations ranged from one tenth to one hundred thousandth molar. We also determined the pH of tap water, boiler water, and double-distilled water by the four methods. Leather extracts and chlorine solutions were studied as examples of reducing and oxidizing agents. The results of these measurements are shown in table 1.

TABLE 1.—pH *values of solutions of various concentrations obtained by different methods*

	Hydrogen electrode	Quinhydrone electrode	Glass electrode	Isohydric indicator method
M/10 NaHPh	3.93	3.93	3.92	3.90
M/100 NaHPh	4.05	4.06	4.04	4.05
M/1,000 NaHPh	4.34	4.37 to (4.33)	4.35	4.30
M/10,000 NaHPh	4.85	4.82 to (4.72)	4.84	4.90
M/100,000 NaHPh	5.68 to (5.95)	5.34 to (5.20)	5.61	5.70
Tap water	8.42 to (8.98)	7.11	7.58	7.70
Boiler water	11.74	(a)	11.52	11.70
Double distilled water	6.18 to (7.66)	6.05 to (5.71)	6.57	6.50
Leather extract	5.28	5.40	5.25	(b)
M/100 buffer containing 0.07 g chlorine per liter [c]	4.59	4.66	4.72	(d)
M/100 buffer containing 1 g chlorine per liter [e]	(f)	0.20	1.90	(d)

[a] Solution too alkaline for quinhydrone electrode.
[b] Solution too deeply colored for indicator method.
[c] This solution was prepared by diluting 50 ml of *M*/20 KHPh-NaOH solution (pH=4.80) and 5 ml of saturated chlorine water (pH=1.71) to 250 ml.
[d] Indicator faded quickly.
[e] This solution was prepared by passing chlorine gas into *M*/100 KHPh-NaOH solution (pH=4.80).
[f] Solution removed plating from electrode.

In making measurements, all at about 25 C, 5 mm by 10 mm gold sheets plated with palladium sponge were used as hydrogen electrodes; 5 mm by 10 mm gold plates were used with the quinhydrone; and saturated calomel electrodes were used as reference standards. No correction was made for the contact potentials which were of course constant in the comparisions of the emf given by hydrogen, glass, and quinhydrone electrodes in any given buffer. The usual sulphonphthalein indicators adjusted in pH values were employed.[7]

It is to be observed that when tap water, distilled water, or other solutions containing carbonates were measured with the usual hydrogen electrodes the escaping hydrogen removed carbon dioxide and the pH rose in one half hour from the initial values stated to those shown in the parentheses in table 1, and was still rising at the end of that time. Solid quinhydrone added to a very dilute acid solution slowly dissolved and because of the weak acidic properties of this oxidation-reduction reagent the pH gradually decreased in about one half hour from the initial value stated to a constant reading given in the parentheses in table 1. Leather extracts gave the same

[7] See reference 3, p. 68.

readings with the glass and hydrogen electrodes, but the quinhydrone electrode and the indicator method were found inapplicable in confirmation of other workers,[8] especially Pleass, and Wallace and Beek. Chlorine present in *M*/100 sodium acid phthalate to the extent of only 0.07 g per liter decolorized the indicator and gave drifting emf readings in the hydrogen and quinhydrone electrodes which became constant at distinctly low values when the chlorine was consumed. When chlorine was present to the extent of 1 g per liter the palladium sponge was dissolved from the hydrogen electrode and the quinhydrone method gave large errors. It was observed, however, that no such drifts or uncertainties arose in this work with the glass electrode even in very dilute solutions and water. Table 2 shows the precision of successive emf readings made on the same solution in the glass electrode at about 1-minute intervals after rebalancing each time. Practically identical results were obtained with fresh portions of the solution placed in the electrode and hence polarization errors may be considered negligible. Table 2 shows the average and maximum deviations from the mean values. As Thompson emphasized, the glass electrode should be recalibrated at least daily against one or more standard buffer solutions.

TABLE 2.—*Average emf values and average and maximum deviations for various solutions in the glass electrode*

Solution	Average of five readings	Average deviation from mean	Maximum deviation from mean	Solution	Average of five readings	Average deviation from mean	Maximum deviation from mean
	Volts	*Volts*	*Volts*		*Volts*	*Volts*	*Volts*
M/10 NaHPh	+0.0439	0.0001	0.0003	Tap water	−0.1696	0.0006	0.0016
M/100 NaHPh	+.0372	.0003	.0005	Boiler water	−.4003	.0006	.0016
M/1,000 NaHPh	+.0188	.0004	.0006	Double-distilled water	−.1113	.0010	.0018
M/10,000 NaHPh	−.0106	.0001	.0001	Leather extract	+.0492	.0003	.0004
M/100,000 NaHPh	−.0551	.0005	.0014	Buffer containing chlorine [a]	−.0039	.0004	.0006

[a] This solution was prepared by diluting 50 ml of *M*/20 KHPh—NaOH solution (pH=4.80) and 5 ml of saturated chlorine water (pH=1.71) to 250 ml.

IV. SUMMARY

In summarizing the results of this work the following conclusions may be drawn.

1. The hydrogen electrode appears to be applicable in solutions whose concentrations are one ten-thousandth molar or greater. It is not generally suitable for determining the pH of distilled water or tap water. In the case of tap water the difficulty may be a disturbance of the carbonate-bicarbonate ratio rather than too low a concentration of electrolyte. The hydrogen electrode is suitable for determining the pH of the boiler water used in this work, but may not be for all boiler waters. Oxidizing and reducing agents may give erroneous results.

2. The quinhydrone electrode is not reliable in solutions whose concentrations are less than one-thousandth molar. This combined with its inapplicability in solutions having a pH greater than 8.5 or containing oxidizing agents or other compounds acting on the quinone or hydroquinone, makes it less satisfactory than the other methods studied.

[8] Pleass, J. Soc. Chem. Ind., *48*, p. 152T, 1929; E. L. Wallace and John Beek, Jr., B.S.Jour. Research vol. 4, p. 737, 1930.

3. The glass electrode appears to be applicable throughout the entire range of concentration from one-tenth molar to double-distilled pH 7 water, with an accuracy of 0.1 pH or better. The solubility of Corning 015 glass is low enough to prevent errors even with distilled water, especially if the solution is flowed through the electrode or kept in it only long enough for measurements.

The glass-electrode method would therefore seem to be valuable as an alternative and hence an electrometric check upon the isohydric-indicator technique in these extremely dilute solutions. It is also generally useful for solutions which are turbid, highly colored or containing oxidizing or reducing agents.

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ANALYSIS OF WOOL-COTTON TEXTILES

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ABSTRACT

The results of a study of several methods for the determination of cotton and wool in mixtures are presented. The inadequacy of some of the methods is shown, and a satisfactory procedure is described. In this method, sizing, finishing materials, and natural nonfibrous constituents of the textiles are removed by solvent extraction followed by digestion with a starch-hydrolyzing enzyme and washing. Wool is determined directly by weighing after removal of the cotton by carbonization with aluminum chloride. Cotton is determined directly by weighing after removal of the wool with potassium hydroxide. Results accurate within 1 percent of the amount of total dry fiber present are readily obtainable by the method.

CONTENTS

		Page
I.	Introduction	75
II.	Materials	77
III.	Determination of sizing, finishing, and other nonfibrous materials	77
IV.	Removal of cotton from mixtures with wool	79
V.	Removal of wool from mixtures with cotton	82
VI.	Proposed method for the analysis of wool-cotton mixtures	83
	1. Drying and weighing	83
	2. Total sizing, finishing, and other nonfibrous materials	83
	3. Determination of cotton cellulose	84
	4. Determination of wool	84
VII.	Analysis of mixtures of known composition by the proposed method	85

I. INTRODUCTION

As a result of the trade-practice conference of the knit-underwear industry held on May 26, 1930, a ruling was adopted by the Federal Trade Commission requiring that "the word 'wool' shall not be used in any way in the labeling, advertising, merchandising, or selling of knit underwear unless the percentage by weight of wool contained in the garment is stated."[1] Further, a commercial standard for "Wool and part-wool blankets" was established by the joint action of producers, distributors, and users, and became effective April 1, 1933. It provides for the labeling of part-wool blankets with the guaranteed minimum wool content.[2] These standardization activities suggested the need for a precise quantitative method of analysis for part-wool textiles.

[1] Statement by the Commission, Trade Practice Conference, Knit Underwear Industry. Mimeographed. July 7, 1930. Federal Trade Commission, Washington, D.C.

[2] CS39-32. Wool and Part-Wool Blankets. Government Printing Office, Washington, D.C., price 5 cents.

In general, textiles made from mixtures of cotton and wool are composed of: (1) Wool fiber (protein); (2) cotton fiber (cellulose); (3) natural oils, waxes, and other constituents of the raw fibers which have not been removed completely in the course of manufacture of the textile; (4) oils, soaps, waxes, starches, clay, and other materials which have been added, collectively termed sizing and finishing materials; and (5) degraded protein and cellulose resulting from chemical deterioration of the fibers before or during processing. The materials named under (3), (4), and (5) are included in the term "nonfibrous materials" subsequently used in this paper.

The usual procedure of the analyst called upon to determine the cotton and wool content of the mixture is to remove nonfibrous material from a weighed specimen of the textile, then to remove one of the fibers by chemical means, and finally to weigh the residue. The weight of the fiber which has been removed from the mixture is then determined by difference. Sometimes allowance is made for materials which are considered to be a normal or allowable part of the fiber but which are removed by the reagents.

Two procedures are in general use for the removal of nonfibrous constituents: One consisting in successive treatments with hydrochloric acid and sodium carbonate, here designated the "scouring" method; the other consisting in a treatment with a hydrolytic enzyme, or the "malting" method. The scouring method was prescribed until recently by the American Society for Testing Materials and for the testing of U.S. Government purchases of wool-cotton textiles.[3] [4] The malting method is the tentative-standard procedure of the American Association of Textile Chemists and Colorists for the determination of sizing, loading, and finishing materials in cotton textiles.[5] It has been shown to give more reliable results than the scouring method.[6]

Two methods are in use for the quantitative separation of the fibers after removal of nonfibrous materials. One depends upon the removal of the cotton either by solution in strong sulphuric acid or by carbonization with aluminum chloride. The other depends upon the removal of the wool by treatment with sodium- or potassium-hydroxide solution.

Few quantitative data have been published to show the effect upon wool protein or cotton cellulose of the various reagents used to effect separation of wool and cotton fibers. It is known that cotton which has been treated with hydrochloric acid loses weight in the potassium-hydroxide solution used to remove wool. It is also known that wool absorbs sulphuric acid and other substances from solutions in which it is immersed. It seemed essential, therefore, to make a quantitative study of the methods for the analysis of wool-cotton textiles in order to establish on an experimental basis a procedure satisfactory for the new demands. That is the purpose of the work reported here.

[3] A.S.T.M. D276-31T. Tentative Methods for Identification of Textile Fibers and Their Quantitative Determination in Mixed Goods. Proc. Am. Soc. Testing Materials, vol. 30, part I, p. 1027, 1931.

[4] U.S.G.M.S. no. 345a. General Specification for Textile Materials (Methods of Physical and Chemical Tests). 1929. Government Printing Office, Washington, D.C. Superseded by F.S. no. CCC-T-191, Textiles; Test Methods. Government Printing Office, Washington, D.C.

[5] Tentative Method for Determination of Total Sizing and Finishing Materials in Textiles. 1931 Year Book Am. Assoc. Textile Chemists and Colorists, pp. 136–137. Howes Publishing Co., New York.

[6] D. A. Clibbens and A. Geake, The Determination of Total Size or Filling in Cotton Goods. Jour. Textile Inst., vol. 22, p. T465, October 1931.

II. MATERIALS

The cotton used in most of the experiments to be described was prepared from "grey" cotton yarn, unbleached airplane cloth, and commercial sheeting, by the method of Corey and Gray for the preparation of high-grade cellulose.[7]

The cotton was extracted 6 hours in a soxhlet apparatus with ether and 16 hours with alcohol. It was allowed to dry in air at room temperature and was then extracted with a boiling 1-percent solution of sodium hydroxide. This extraction was carried out in a 500 ml erlenmeyer flask fitted with a siphon, and the extraction rate was so regulated that 10 l of solution was used in 4 hours. During the treatment the cotton was not allowed to come in contact with the air and the solution in the flask was kept boiling. After the caustic treatment the material was rinsed with water, the residual alkali was neutralized with 5 percent acetic acid, and the material was then rinsed with water until neutral to methyl red.

The wool was prepared from raw wool, commercial yarns, and cloth. The visible foreign material was removed from the raw fiber by hand. The wool was then agitated in a 1-percent solution of a neutral soap for ½ hour at 70 C, rinsed well with distilled water at the same temperature, extracted in a soxhlet extraction apparatus with alcohol for 16 hours and then with ether for 6 hours. It was then air dried, rinsed once with distilled water at 70 C to remove residual traces of alcohol,[8] and dried in a well-ventilated oven at 60 C for about 2 hours.

For some of the experiments, the wool and cotton yarns and cloths were used as received from the manufacturer.

III. DETERMINATION OF SIZING, FINISHING, AND OTHER NONFIBROUS MATERIALS

A consideration of the variety and ever-increasing number of materials applied to textiles in the form of sizing, filling, or coating for the purpose of improving their appearance or "feel", increasing their weight, or rendering them resistant to water, organisms, fire, etc., leads to the conclusion that no practicable method is possible for the quantitative removal of all nonfibrous materials that may be present. The analyst must adapt any standard method to the material in hand. However, for the more usual wool-cotton textiles that come to the laboratory for analysis, particularly for blankets and underwear, a satisfactory standard method seems possible.

Adequate methods for the quantitative determination of materials added to the fiber in the course of manufacture or for nonfibrous natural constituents which have not been completely removed in the processing, are still to be developed. For this reason, and also because it makes little difference to the consumer of the finished article whether the nonfibrous materials are natural or added, it is logical to consider all such substances as a group for the purpose of analysis.

Specimens weighing about 10 g each of the yarns and cloths were dried in an oven at 105 to 110 C to constant weight. They were

[7] A. B. Corey and H. Le B. Gray, Notes on the Preparation of Standard Cellulose. Ind. Eng. Chem., vol. 16, p. 853, August 1924.

[8] R. T. Mease, Adsorption of Alcohol by Fibrous Materials. Ind. Eng. Chem., Anal. Ed., vol. 5, p. 317 September 15, 1933.

then treated by the method for the removal of sizing and other nonfibrous materials, dried as before, and the change in weight determined.

The scouring method involved the following steps: (1) Extracting the fibers with ethyl ether in a soxhlet apparatus for 1 hour; (2) immersion in boiling distilled water for 10 minutes; (3) immersion in 0.5-percent solution of sodium carbonate (Na_2CO_3) at 90° to 95° C. for 30 minutes; (4) rinsing with distilled water; (5) immersion in 0.5-percent solution of hydrochloric acid for 30 minutes; (6) rinsing in distilled water; (7) rinsing in 1-percent solution of sodium carbonate; and (8) rinsing in distilled water.

In the malting method, the specimens were extracted with chloroform (some with carbon tetrachloride) in a soxhlet apparatus for 2 hours, allowed to dry in the air, and washed with hot water. They

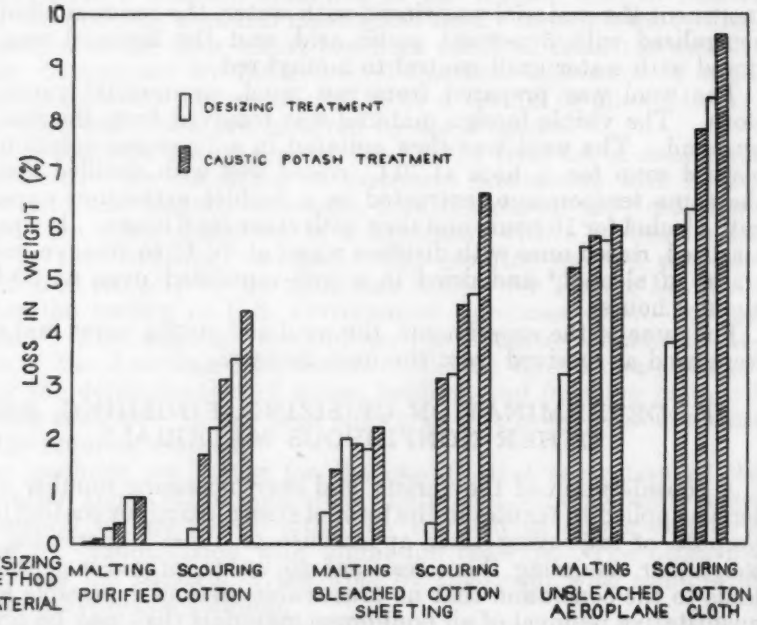

FIGURE 1.—*Change in weight of cotton specimens subjected to desizing and caustic treatments.*

[The loss in weight of a specimen after desizing, desizing and treatment with caustic potash, and repetition of these treatments 1 and 2 times is shown.]

were then placed in a 0.5-percent water solution of a starch-hydrolyzing enzyme at 50 C, and squeezed to remove air and insure wetting of the fibers. The solution was then heated to 70° C. and the specimens kept immersed in it at this temperature for 15 minutes.

The effects of these treatments on the weight of cotton when applied 1, 2, and 3 times in succession are shown in figure 1 and their effects on the weight of wool shown in figure 2. Each desizing treatment of the cotton was followed by a caustic-potash boil required by one method of analysis for the removal of wool. The total loss in weight of the specimens caused by the treatments is shown in figure 1. It is evident that the scouring method leaves cotton cellulose more susceptible to attack in the caustic treatment necessary to remove wool than does the malting method of desizing. The

malting method has much less effect on wool than the scouring method. Neither purified cotton nor purified wool loses more than a few tenths of a percent of its weight in a single treatment. Figure 2 shows that successive malting treatments produce a small increase in weight of wool cloth that has not been subjected to the purification process. Though the increase in weight of the commercial wool cloth and the decrease in weight of the purified wool when subjected to the malting treatment are unimportant for ordinary analytical purposes, they may be significant for other work.

IV. REMOVAL OF COTTON FROM MIXTURES WITH WOOL

One published method for the removal of cotton from mixtures with wool calls for treatment of the specimen with a solution of sulphuric acid prepared by mixing 80 ml of the concentrated laboratory reagent with 25 ml of water and weighing the wool residue after it is washed and dried.[9] This method may be applied to the fiber mixture free from sizing and finishing materials or, if these materials are removed by the sulphuric-acid solution, it may be applied directly to a specimen of the original material. A similar method for separating cotton and rayon from wool is recommended by Krais and Markert.[10]

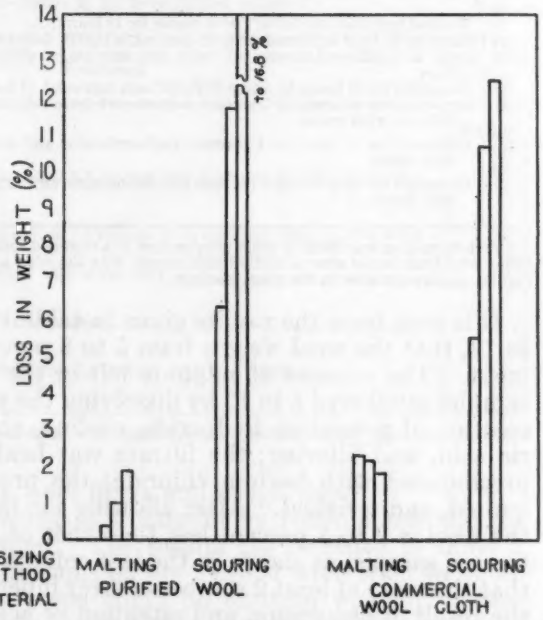

FIGURE 2.—*Change in weight of wool specimens subjected to desizing treatments.*

[The change in weight of a specimen after desizing 1, 2, and 3 times is shown.]

Though cotton is readily dissolved by the acid, it was thought necessary to determine whether the wool is recovered quantitatively. Skeins of purified wool were dried, weighed, and then immersed for 15 minutes in 80 to 100 times their weight of sulphuric-acid solution at room temperature. The wool was then washed until the wash water gave no test for acid with methyl red indicator or for sulphate with barium-chloride solution. It was finally dried and weighed.

[9] Roger Castle Griffin, Technical Methods of Analysis, p. 506, 2nd ed. 1927. McGraw-Hill Book Co., Inc., New York.

[10] P. Krais and H. Markert, Quantitative Determination of Cotton, Wool, Silk, and Artificial Silks in Mixed Textiles. Jour. Textile Inst., vol. 23, p. 214, August 1932.

TABLE. 1.—*Changes in weight of cleaned wool treated with sulphuric acid*

Sample no.	Treatment	Gain in weight	Loss in weight when corrected for absorbed SO_4
		Percent	*Percent*
1	Washed with water at room temperature until water gave no test for acid or SO_4.	7.0	
2		5.1	
3		5.7	
4		6.8	
5		6.5	
6		6.2	
7		5.5	
8		7.8	2.5
9		7.4	2.3
10		8.4	3.0
11		8.7	2.6
12		8.8	2.4
13	Washed and then extracted [1] with water for 10 hours	5.9	
14	Same as 13, then extracted with 0.2 percent NH_4OH, followed by water	5.7	
15	Same as 14, followed successively with soap solution, an alcohol, and an ether rinse.	5.4	
16	Immersed for 16 hours in dilute NH_4OH and extracted 10 hours with water	6.9	
17	Immersed for 16 hours in 1 percent sodium-carbonate solution and extracted 10 hours with water.	6.0	
18	Immersed for 16 hours in 1 percent triethanolamine and extracted 10 hours with water.	9.9	
19		8.9	
20		7.6	
21	Immersed for 16 hours in 2 percent triethanolamine and extracted 10 hours with water.	7.4	

[1] Each extraction was made at room temperature in a modified soxhlet apparatus, the extraction chamber filling with fresh liquid after each discharge, except with the ether and alcohol—these were made with the regular soxhlet extractor in the usual manner.

It is seen from the results given in table 1, for samples numbered 1 to 12, that the wool weighs from 5 to 8 percent more after this treatment. The amount of sulphate left in the wool was determined for samples numbered 8 to 12 by dissolving the yarn in a boiling 5-percent solution of potassium hydroxide, cooling, acidifying with hydrochloric acid, and filtering; the filtrate was heated and the sulphate ion precipitated with barium chloride; the precipitate filtered, washed, ignited, and weighed. After allowing for the sulphate, the weight of the wool is 2 to 3 percent less than that of the original, cleaned, untreated sample, as shown in the last column of the table. It appears that there are at least 2 sources of error inherent in the method. One, the result of absorption and retention of acid by the wool; the other, the result of partial decomposition of the wool in the acid treatment.

An effort was made to eliminate the absorbed sulphate by various treatments without serious decomposition of the wool itself, but none was successful. The results of these experiments are also given in table 1, samples 13 to 21. They show that the sulphuric-acid method as commonly applied to the quantitative separation of wool and cotton or rayon gives inaccurate results because a proper correction is not made for the absorbed acid which is not removed from the wool. The results for wool may be high by as much as 8 percent of the amount actually present.

A modification of the commercial process of carbonization with aluminum chloride has been adopted by some industrial laboratories for the removal of cotton from mixtures with wool. The laboratory method first brought to our attention included the following steps:

1. Boil about 1 g of the fiber mixture for 10 minutes in a 5-percent aqueous solution of aluminum chloride.

2. Remove the fibers from the aluminum chloride solution without squeezing and bake them for 2 hours on a watch glass in an oven at a temperature of 100 to 105 C.

3. Rub the fibers well between the hands over a piece of smooth glazed paper to break up the hydrated cellulose and to separate as much of it as possible from the wool.

4. Collect the hydrated cellulose in a flask and shake it with an aqueous solution of hydrochloric acid. Let the suspension stand for a few minutes and then wash it through a no. 100 sieve with tap water. The hydrated cellulose passes through and any wool fibers mixed with the cellulose will remain on the sieve. Collect the wool fibers and wash them with 10-percent hydrochloric-acid solution. Filter through the sieve and rinse well with tap water.

TABLE 2.—*Changes in weight of cleaned wool treated by the different steps of the aluminum-chloride carbonization method* [1]

Sample no.	Treatment	Change in weight
		Percent
20	Baked at 100° to 105° C.; washed with 3.5 percent HCl, 2 percent Na_2CO_3, and water	−0.6
21		−.5
22		−.5
23		−.6
24		−.8
25	Baked at 105° to 110° C.; washed with 3.5 percent HCl, 2 percent Na_2CO_3, and water	−.7
26		−.5
27	Baked at 105° to 110° C.; washed with water only	2.3
28		1.8
29		2.4
30	Treated with 3.5 percent HCl and washed	.1
31		.0
32		.0
33	Baked at 105° to 110° C; washed with 3.5 percent HCl, and water	−.2
34		−.3
35		.0

[1] Values are in percentages of the oven-dried wool and represent increases except where preceded by a minus sign.

5. Dry or condition the wool fibers and weigh them.

Purified wool was subjected to treatment by this method and the change in weight determined. The results are recorded in table 2, samples 20 to 24. Modifications of the method were tried to determine whether any of the steps could be omitted without causing greater changes in the weight of cleaned wool treated. The results on samples 25 and 26 show that the baking temperature may be raised to 105 to 110 C so that the same oven used by laboratories for drying fibers to constant weight at this temperature may also be used for baking the specimen for carbonization. Washing the wool fibers with hydrochloric-acid solution is necessary for the removal of decomposition products of the aluminum salt which may otherwise be retained by the wool fibers, producing errors in the weight for wool. This is illustrated by the results obtained on samples 27 to 29, which were not washed with acid. Wool fibers given the treatment received by this group of samples yield a considerable ash on ignition. It seems, however, that the treatment with 2-percent sodium-carbonate solution may be successfully omitted, samples 30 to 32. It is probable that this treatment was introduced with the object of neutralizing any hydrochloric acid that might be held by the wool so that it could be more readily removed. Wool treated at room temperature with

approximately 3.5-percent solution of hydrochloric acid (prepared by diluting 1 part of the concentrated laboratory reagent acid (35 to 36 percent) with 9 parts of distilled water), to remove the decomposition products of aluminum chloride, can readily be washed free of acid with practically no change in weight of the wool treated. This is shown by the results obtained on samples 30 to 32.

These results show that the aluminum-chloride carbonization method for removing cotton from wool, as given above, produces changes in weight of purified wool of less than 1 percent of the weight of the wool treated; that the method may be modified by baking at 105 to 110 C instead of 100 to 105 C to suit the convenience of the analyst; and that the treatment of the wool residue with 2-percent sodium-carbonate solution may be omitted.

No difficulty was experienced in collecting the wool fibers during the rubbing-out process to remove the carbonized cellulose. With the aid of a no. 40 wire sieve placed between the hands and glazed paper the dry wool and cotton can be easily separated and the wool obtained in the form of a tangled mass or mat. Washing the cellulose with hydrochloric acid as described in the first part of step 4 can be omitted. It was further observed that when wet wool fibers are placed upon a no. 100 sieve, some of the ends of the fibers extend to the opposite side and become quite firmly held in the meshes. This screen is not considered satisfactory. A small büchner funnel or gooch crucible was found very convenient and effective for holding the wool fibers while washing them to remove aluminum salts.

With the modifications suggested, the method is convenient and applicable for the accurate determination of wool in mixtures with cotton and regenerated cellulose rayons, but not with cellulose acetate. The regenerated cellulose rayons, like cotton, are carbonized by the treatment. Many of the common sizing and finishing materials are likewise removed.

V. REMOVAL OF WOOL FROM MIXTURES WITH COTTON

The fact that wool is readily dissolved by hot caustic solution has been the basis of quantitative methods for separating wool from cotton. The residual cotton is weighed and the amount of wool is estimated from this weight and that of the untreated specimen. It has been customary to make an arbitrary correction on the weight of cotton residue obtained to allow for natural noncellulosic materials likely to be present in it. It seems preferable for purposes of analysis to consider "cotton" and "cotton cellulose" as synonymous terms. Any allowances that may be desired may conveniently be based upon this weight.

Specimens of purified cotton—some of it in the form of yarns and some as unspun fibers—were subjected to the treatment for removal of wool; that is, immersion for 15 minutes in a boiling 5-percent solution of potassium hydroxide. Care was taken to keep the specimen submerged and increased concentration of the solution by evaporation was avoided by use of a reflux condenser. The cotton was then rinsed with water, then with 1-percent aqueous solution of acetic acid and again with water until neutral to methyl-red indicator. Figure 1 shows the loss in weight of purified cotton, unbleached and bleached cotton when subjected to desizing treatments followed by a boiling

caustic-potash solution to remove wool. It was found that purified cotton cellulose lost no appreciable weight when subjected to a malting followed by a caustic-potash treatment. Bleached and unbleached cotton lost much more. This can only be accounted for by the presence of materials other than cotton cellulose. The amount lost indicates the magnitude of error for wool when it is determined by difference.

When cotton cellulose only is to be determined, a preliminary extraction and malting treatment to remove size and finishing materials may not be necessary; the results show, however, that a specimen used for determination of size and finishing materials by the malting method may also be used for the determination of cotton cellulose.

VI. PROPOSED METHOD FOR THE ANALYSIS OF WOOL-COTTON MIXTURES

Wool and cotton fibers may be separated mechanically and determined with the aid of a microscope and proper auxiliary equipment.[11] [12] Such separation is easily made if the wool and cotton are in separate yarns in a fabric, but is tedious and less reliable if the fibers are spun together into yarns. If a method of counting the fibers is used, computations must be made to take into account the relative diameters and densities of wool and cotton fibers if the results are to be expressed on either a volume or weight percentage basis. The following method of chemical analysis is proposed for use where mechanical methods for separation of the fibers are inconvenient or impractical.

1. DRYING AND WEIGHING

Dry 5 g of the material in an oven maintained at 105 to 110 C (221 to 230 F) to constancy ±0.1 percent of the weight of the specimen. A satisfactory procedure is to dry the specimen for 1½ hours, remove it from the oven, place it while warm in a tared weighing bottle, cover, cool in a desiccator, and weigh; return the specimen to the oven and repeat the drying and weighing until constant weight is attained. Let the weight of the oven-dried sample be called A.

2. TOTAL SIZING, FINISHING, AND OTHER NONFIBROUS MATERIALS

(*a*) The purpose of this procedure is to remove nonfibrous natural constituents and materials added by the manufacturer, such as starch, china clay, soap, some waxes, and some nondrying oils. However, general directions for the removal of all substances which may be present cannot be given. When it is necessary to modify the procedure in order to remove nonfibrous constituents completely, the analyst should make certain that purified fibers do not lose weight, or are not made susceptible to loss when analysed for fiber content according to the modified procedure.

(*b*) Extract the dried specimen from 1 in a soxhlet apparatus for 2 hours with carbon tetrachloride. Allow the specimen to dry and then wash it by alternate immersion in hot distilled water and by squeezing.

[11] Edward R. Schwarz. Microscope is valuable asset to textile manufacturer and finisher. Textile World vol. 80, p. 770, Aug. 29, 1931.

[12] Heermann, Paul, und Herzog, Alvis, Mikroskopische und Mechanischtechnische Textiluntersuchungen, p. 216, 3d ed., 1931. Julius Springer, Berlin.

(*c*) Immerse the specimen in a 0.5-percent aqueous solution of a starch-hydrolyzing enzyme at 50 C (122 F), squeeze the specimen while it is immersed, then remove and squeeze it again.[13] This procedure is repeated with the same solution for a total of three times to saturate the fibers. The enzyme solution is then maintained at 70 ± 1 C (158 F) and the specimen kept immersed in it for a period of 15 minutes. Rinse the specimen 12 times in fresh portions of hot distilled water, squeeze it after each rinse, and dry it to constant weight as before. This gives the weight of dry fiber, called *B*. The percentage of sizing, finishing, and other nonfibrous materials in terms of the weight of the oven-dried specimen is $100\frac{A-B}{A}$. Care must be taken at all times not to wash away any fibers.

3. DETERMINATION OF COTTON CELLULOSE

Place the specimen from 2 (*c*) in a boiling 5-percent aqueous solution of potassium hydroxide [14] (previously boiled to remove dissolved air) for 10 minutes; sufficient solution is taken to cover the specimen continually. Decant or filter the solution and rinse the cotton residue with hot distilled water, then with a 5-percent aqueous solution of acetic acid, and finally with water until the rinse water is neutral to blue litmus paper. The residue is dried and weighed, giving weight *C*. This is the weight of dry cotton cellulose in the specimen. Then the percentage of cotton in the dried specimen is $100\frac{C}{A}$.

4. DETERMINATION OF WOOL

(*a*) This method is applicable to the determination of wool in mixture with cotton, regenerated cellulose rayons, or both. It is not applicable to mixtures containing cellulose acetate or silk.

(*b*) Treat a specimen of the material as described under 1, 2 (*b*), and 2 (*c*), but omit the weighing under 2 (*c*). Immerse the specimen from 2 (*c*) for 10 minutes in a boiling solution of aluminum chloride prepared by dissolving 9 g of the hydrated salt ($AlCl_3 6H_2O$) in 100 ml of water. Remove the specimen from the solution; allow the excess liquid to drain or the specimen may be lightly squeezed. Heat it at 105 to 110 C (221 to 230 F) until the cotton has become brown and brittle—2 hours is usually sufficient. Hold the specimen over a piece of glazed paper and work it with the hands in order to pulverize the carbonized cellulose and separate it from the wool. By suitable manipulation, all of the wool is obtained as a mat and the cellulose is left on the paper, mostly in the form of a powder. The separation is facilitated by the use of a wire screen, approximately no. 40, between the hands and the glazed paper. Place the wool in a beaker of warm water, agitate it thoroughly to wet it, and form a mat of the coarser fibers in a gooch crucible or büchner funnel; apply gentle suction and pour the remaining fibers and filtrate on the pad. Remove the fibers and agitate them with a solution of hydrochloric acid prepared by diluting 1 part of the concentrated laboratory acid

[13] The effectiveness of the hydrolytic action of the enzyme should always be tested when in doubt. This may be done by treating fabric or yarn, known to contain starch sizing, with the enzyme solution according to the method prescribed and then testing for starch with iodine. This may be done by placing the fibers in a straw-colored aqueous solution of iodine. The fibers should not be blue after 5 minutes immersion.

[14] Although potassium hydroxide is preferred for critical work, sodium hydroxide is probably satisfactory for ordinary purposes.

with 9 parts of distilled water. Repeat the operation using several portions of water instead of acid until the wool is freed from powdered cellulose and the wash water is free from chlorides. The wool is dried to constant weight, called D. Then the percentage of wool in the specimen is $100\,\frac{D}{A}$.

A less reliable value for wool may be obtained by difference after the removal of wool according to paragraph 3, by use of the formula $100\,\frac{B-C}{A}$; similarly, cotton or cellulosic material may be determined by the formula $100\,\frac{B-D}{A}$.

VII. ANALYSIS OF MIXTURES OF KNOWN COMPOSITION BY THE PROPOSED METHOD

Table 3 gives the results of analyses to determine the amount of wool in known mixtures of purified cotton and wool. The samples were prepared in the laboratory by drying purified wool and cotton, some as yarns and others as loose fibers, and accurately weighing and then mixing them. They were then analyzed according to the method described in section VI.

TABLE 3.—*Analyses of prepared wool-cotton mixtures for wool content*

Wool content (percent)			
Present	Found	Present	Found
87.9	88.2	49.4	49.1
83.8	83.8	40.1	40.0
78.3	79.0	29.4	29.1
72.8	72.3	20.0	20.3
69.4	69.7	9.9	9.9
57.8	57.7	5.3	5.3

Other samples, prepared similarly, were analyzed for cotton content by the method recommended for cotton by two analysts working independently, one inexperienced in its use. The results of these analyses are given in table 4.

TABLE 4.—*Analyses of wool-cotton mixtures for cotton content*

Cotton content (percent)					
Analyst	Present	Found	Analyst	Present	Found
G	53.0	52.6	J	48.3	47.3
	55.4	55.1		49.3	48.9
	80.1	79.5		18.0	18.0
	80.5	80.0		18.5	18.4
	19.8	19.5		85.4	85.2
	23.6	23.4		83.8	83.6

When mixtures to be analyzed consist of comparatively pure cotton and wool, either one of these may be determined directly as described, and the other by difference, with a fair degree of accuracy. In actual practice, however, fabrics may contain other materials which may introduce an error in the figure for fiber content obtained by difference. This error is usually eliminated if the fiber which is to be determined is weighed directly.

It is not always required that sizing and finishing materials be determined. The aluminum-chloride carbonization method for determining wool and the potassium-hydroxide method for determining cotton may be applied directly to specimens of the original mixture provided extraneous materials are removed by the treatments.

Although the fibers used in these tests did not contain size, they were given the treatment recommended for its removal. Therefore, the results given include the possible error produced. The method gives the amount of cotton and wool in mixtures of these fibers to within 1 percent of the total weight of the fiber present.

WASHINGTON, October 11, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

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A NEW CATHODE-RAY OSCILLOGRAPH AND ITS APPLICATION TO THE STUDY OF POWER LOSS IN DIELECTRIC MATERIALS [1]

By Forest K. Harris

ABSTRACT

A cathode-ray oscillograph is described in which the electron beam, supplied from an incandescent filament, is accelerated in two stages. The beam is formed by a low-voltage accelerating field between the cathode and anode and after being deflected is further accelerated just before it reaches the fluorescent screen. In this way a very bright fluorescent spot is obtained without sacrificing sensitivity. With a cathode-anode voltage of 500 volts and a fluorescent-screen voltage of 5,000 volts the electrostatic sensitivity is 3 mm per volt and there is no difficulty in obtaining instantaneous photographs of 60~ phenomena. A method using the oscillograph for measuring power factor of a dielectric material from a single cycle of alternating stress is developed and analyzed. While this method does not give as precise values as a balanced bridge method of measurement, it may be used to make a continuous record of power loss in a dielectric material for individual cycles of stress at commercial frequencies. It should be useful in studying the phenomena which accompany the electrical failure of the material. It is equally applicable to very large or very small specimens. The limitations and precision of the method are discussed in some detail.

CONTENTS

		Page
I.	Introduction	87
II.	The oscillograph	88
III.	The cathode-ray oscillograph as a power-factormeter	92
IV.	Tests of the apparatus	96
V.	Conclusion	99
VI.	Appendix	100

I. INTRODUCTION

When a dielectric material is subjected to an alternating electrical stress some energy is absorbed and transformed into heat. The power loss is usually very small and special bridge methods and wattmeter methods have been devised for its measurement. These methods require that the power loss be constant during the time required to balance the bridge or read the wattmeter, a minimum of some seconds.

If the dielectric material is in an unstable state and the power loss is changing rapidly the methods ordinarily used for its measurement are inapplicable. Under such circumstances one must use a method which will continuously record changes taking place in the specimen. Such a method has been developed in connection with a study now

[1] This paper includes the subject matter used in a dissertation submitted to the board of university studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of doctor of philosophy. A copy of this dissertation is on file at the library of the university.

in progress on the electrical failure of dielectric materials. A description and analysis of this method are presented in the following pages. The method consists essentially in the use of a capacitance bridge in combination with a cathode-ray oscillograph to continuously record the instantaneous current and voltage at the specimen of insulating material under observation in such a way that its power factor is readily computed.

The data obtained with this method consist of continuous records of power factor of the dielectric for individual cycles of alternating stress. Such records may be continued to the point where failure of the specimen occurs, without injury to the apparatus used and without the need for very special precautions for the protection of the apparatus against the surges accompanying the breakdown.

II. THE OSCILLOGRAPH

The recording element of a cathode-ray oscillograph is an electron beam, generated in a high vacuum and deflected by an electric (or magnetic) field. Electrons, emitted by a cathode, are accelerated toward an anode by a suitable voltage and pass through a small diaphragm, usually a hole in the anode itself, to form the beam. The beam strikes a fluorescent screen and gives rise to a luminous spot. The variations in the deflecting field are recorded by photographing the motion of the luminous spot on the screen. In the present case the figures traced on the fluorescent screen are photographed through a viewing window in the side of the oscillograph tube.

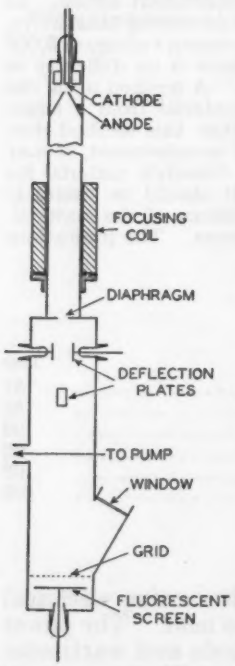

FIGURE 1.—*Diagram of oscillograph.*

The oscillograph described here is a modification of a design due to Rogowski.[2] Modifications incorporated in the design make it possible to obtain a continuous record of 60~ phenomena with a maximum sensitivity of 3 mm per volt difference of potential at the deflection plates.

The oscillograph is shown schematically in figure 1.[3] It is constructed of drawn-brass tubing with the cathode, deflection plates, and fluorescent screen sealed through glass tubes and introduced into the metal chamber through conical ground joints. Picein wax is used to seal both tapered and soldered joints. The outside of the chamber is coated with alternate layers of shellac varnish and nitrocellulose brushing lacquer to insure vacuum tightness throughout.

[2] Rogowski and Grösser; Arch. f. Elektrot., vol. 15, p. 377, 1925.

[3] The oscillograph and the camera used with it were constructed in 1927 in the Bureau's instrument shop by J. M. S. Kaufman and E. A. Tibbals who were also responsible for many of the details of design used in the instrument.

The cathode is an oxide-coated filament surrounded by a metal shield which is held at the same potential as the filament. This shield has a plane surface facing the anode and the small hole in its center is almost completely filled by the filament. The cathode system thus is practically a plane surface having a central hot spot which serves as a source of electrons.

The anode is a cone, pointed toward the cathode, with a small hole at its apex through which the electron beam passes. As a result of the focusing action arising from this point-plane arrangement, an intense beam of electrons passes through the hole in the anode and down the tube.

The electron beam is brought to a focus at the fluorescent screen by means of the coil located midway between the anode and the screen. After going through the field of the focusing coil, the beam

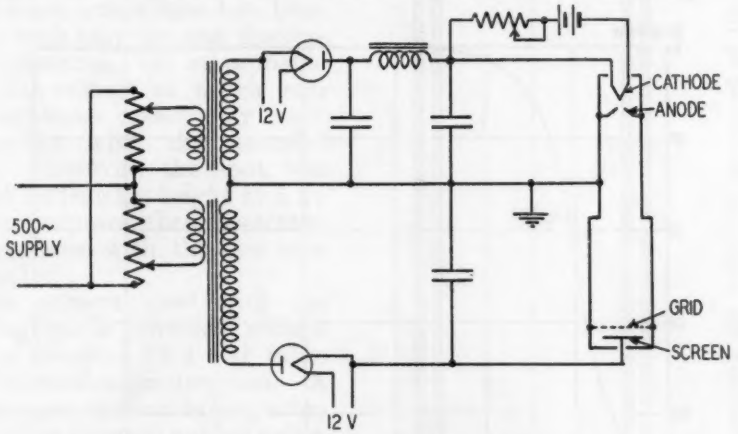

FIGURE 2.—*Voltage supply for oscillograph.*

passes through a diaphragm, between the deflection plates, and through a grid before striking the fluorescent screen.

The fluorescent screen is of finely powdered willemite and calcium tungstate[4] deposited on a roughened aluminum plate. It is insulated from the metal tube which forms the body of the oscillograph in order that an accelerating potential may be applied between the grid and screen. The grid is formed of no. 40 A.W.G. copper wires spaced 1 mm apart and stretched on a metal frame in electrical contact with the metal tube.

The sensitivity (response for unit stimulus) of a cathode-ray oscillograph in which the electron beam is deflected by an electric field between parallel plates is inversely proportional to the voltage used to accelerate the beam. The brightness of the fluorescence caused by the beam is increased toward a limiting value by increasing the beam voltage. The sensitivity resulting from a low voltage beam can be retained and at the same time the fluorescence can be made sufficiently bright to photograph a single trace of a 60~ wave by ac-

[4] A number of different fluorescent materials have been tried. Best results have been obtained by using a mixture of calcium tungstate with two kinds of artificial willemite. These materials were prepared and supplied through the courtesy of Prof. R. H. George of Purdue University. The willemites fluoresce green and yellow, respectively, and the calcium tungstate blue. The mixture used shows a brilliant white fluorescence which is very active photographically.

celerating the beam in two stages, the second acceleration being impressed after the beam is deflected and just before it reaches the fluorescent screen.[5]

Direct accelerating voltage is applied between the cathode and the anode and between the grid and the fluorescent screen by rectifying a 500~ voltage and filtering the resulting pulsating unidirectional voltage to minimize the ripple. A diagram of the supply circuit is shown in figure 2.

The oscillograph will operate with a cathode voltage as low as 500 volts. Usually the voltage impressed between the grid and the fluorescent screen is held at 5 kv, since it has been found that little gain in brightness of the fluorescent screen results from increasing the screen voltage above this value.

The brightness of the fluorescent spot as a function of voltage was investigated in the following manner. The heating current through

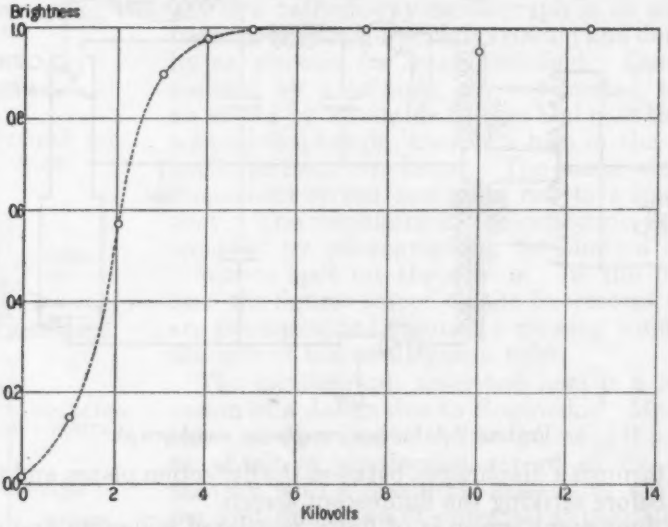

FIGURE 3.—*Brightness of fluorescent screen as a function of grid-screen voltage.*

the cathode and the voltage between the cathode and anode (500 volts) were held constant. This insured a constant supply of electrons reaching the screen and eliminated any variation in the beam density. The voltage between the grid and the screen was varied and the brightness of the fluorescence was measured by comparing the density of photographs of the spot taken at various voltages. A scale of brightness was set up on the same negative by making a second series of exposures while holding the voltage constant and varying the diaphragm opening of the camera. The density was kept within the scale thus provided by using small diaphragm openings when photographing the spot at high voltages where it becomes very bright. The distance of the camera from the screen and the exposure time were held constant throughout, and an entire series was taken on a single film. This minimized the possibility of density

[5] This device has been suggested on several occasions: by W. F. G. Swann (1918); W. Rogowski (1920); A. B. Wood (1923). A tube incorporating this feature has been described by E. Sommerfeld, Arch. f. Elektrot., vol. 20, p. 607, 1928.

variation due to unequal development, unequal film sensitivity, and other related causes. The resulting photographs of the spot were then matched in density against the scale provided by the exposures with graded diaphragm openings.

The average values obtained from two such runs are shown in figure 3 plotted to an arbitrary scale.[6] It is apparent from the figure that no gain is made in the brightness of the fluorescent spot by increasing the voltage beyond 5 kv. This brightness comparison has been made with only the one fluorescent material. It is probable that the voltage at which gain in brightness ceases may vary somewhat with the material used. However, the spot was found sufficiently bright at 5 kv for our purposes when this screen was replaced with the one now in use.[7]

The camera used with the oscillograph is provided with a lens of aperture f:3.5 and takes 35-mm motion-picture film. A continuous motion is imparted to the film through a set of reduction gears operated by a synchronous motor. A friction clutch with a trigger release is incorporated into the driving mechanism so that the motor may be operated continuously and the film set into motion with a minimum of delay. A brake is also provided which operates when the clutch is disengaged and quickly stops the motion of the film. The camera has a magazine holding a 100-foot reel of film, and is so designed that lengths of film up to 20 feet may be exposed and withdrawn. Arrangements are made which permit the extraction of film in full daylight. With the film speed used, continuous records may be made over time intervals up to 45 seconds.

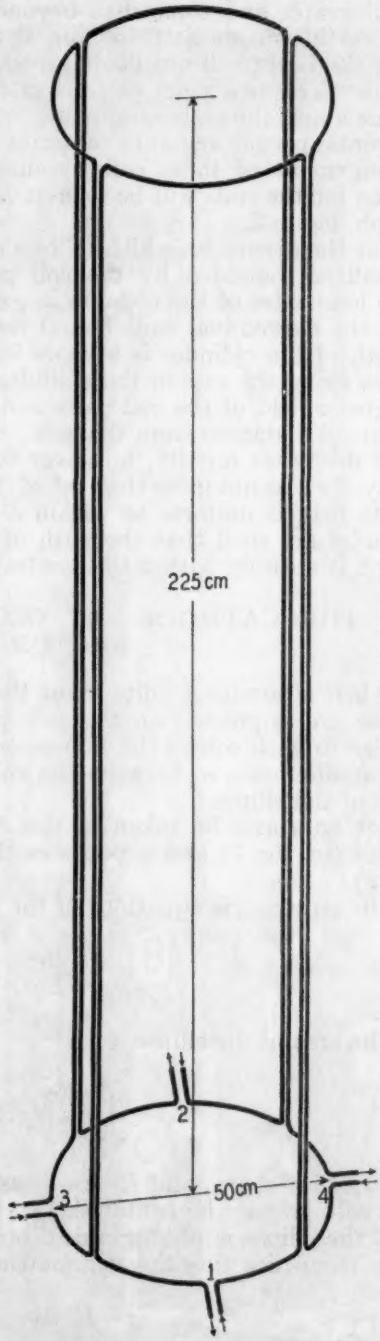

FIGURE 4.—*Diagram of coils for compensating the horizontal component of the earth's magnetic field.*
(Coils 1 and 2 are connected in series to form a pair; coils 3 and 4 form the second pair at right angles. The direction of the current in each coil is indicated by the arrows.)

[6] The material used for this test was a natural willemite from Franklin, N.J., obtained from Dr. Henry S. Washington.

[7] See footnote 4, p. 89.

Two pairs of long narrow coils extending the full length of the oscillograph and somewhat beyond, compensate the component of the earth's magnetic field normal to the axis of the oscillograph so that the beam will not be deflected off the screen by the earth's field alone. The two pairs of coils at right angles to each other form a frame about the oscillograph and, by independent adjustment of their currents, permit accurate centering of the beam on the screen. The arrangement of these coils is shown in figure 4. The supporting frame for the coils will be seen at D in the photograph of the oscillograph, figure 5.

For the discussion which follows a vertical circular cylinder may be visualized, bounded by the coil pairs and their supporting frame. The long sides of the coils lie in generating elements of this cylinder and the curved coil ends bound right sections of the cylinder. The length of the cylinder is 9 times its radius. For a considerable distance along the axis of the cylinder the horizontal component of the magnetic field of the coil pairs is quite uniform and varies but little for small distances from the axis. Near the ends of the cylinder the field decreases rapidly, but over 0.8 of its length and for distances away the axis not more than 0.1 of its radius the horizontal component of its field is uniform to within 5 percent. The dimensions of the cylinder are such that the path of the electron beam in the oscillograph is entirely within this central zone.[8]

III. THE CATHODE-RAY OSCILLOGRAPH AS A POWER-FACTOR METER

When alternating voltages of the same frequency but differing in phase are impressed on the two pairs of deflection plates at right angles to each other, the fluorescent spot describes an ellipse. The phase difference, α, between the voltages is readily deduced from the area of the ellipse.[9]

Let an x-axis be taken in the direction of one pair of deflection plates (cd, fig. 7) and a y-axis in the direction of the other pair (ab, fig. 7).

The parametric equations of the ellipse are

$$\begin{aligned} x &= E_1 \cos(\omega t + \alpha) \\ y &= E_2 \cos \omega t \end{aligned} \tag{1}$$

The area of the ellipse is

$$A = \int_{\omega t=0}^{\omega t=2\pi} y\,dx = \pi E_1 E_2 \sin \alpha \tag{2}$$

Hence, if A, E_1, and E_2 are measured the phase difference between the voltages can be computed.

If the ellipse is photographed on a film moving at constant speed, p, in the x-direction the parametric equation for x is modified to

$$x = E_1 \cos(\omega t + \alpha) + pt$$

[8] The analysis leading to this result is too extensive to be presented here appropriately. A solution of the normal field component at the axis of such a cylinder is given by Beyerle; Arch. f. Elektrot., vol. 25, p. 209, 1931. The solution due to Beyerle is not complete but shows the method by which the problem may be attacked.

[9] Minton; Trans. A.I.E.E., vol. 34, p. 1627, 1915.

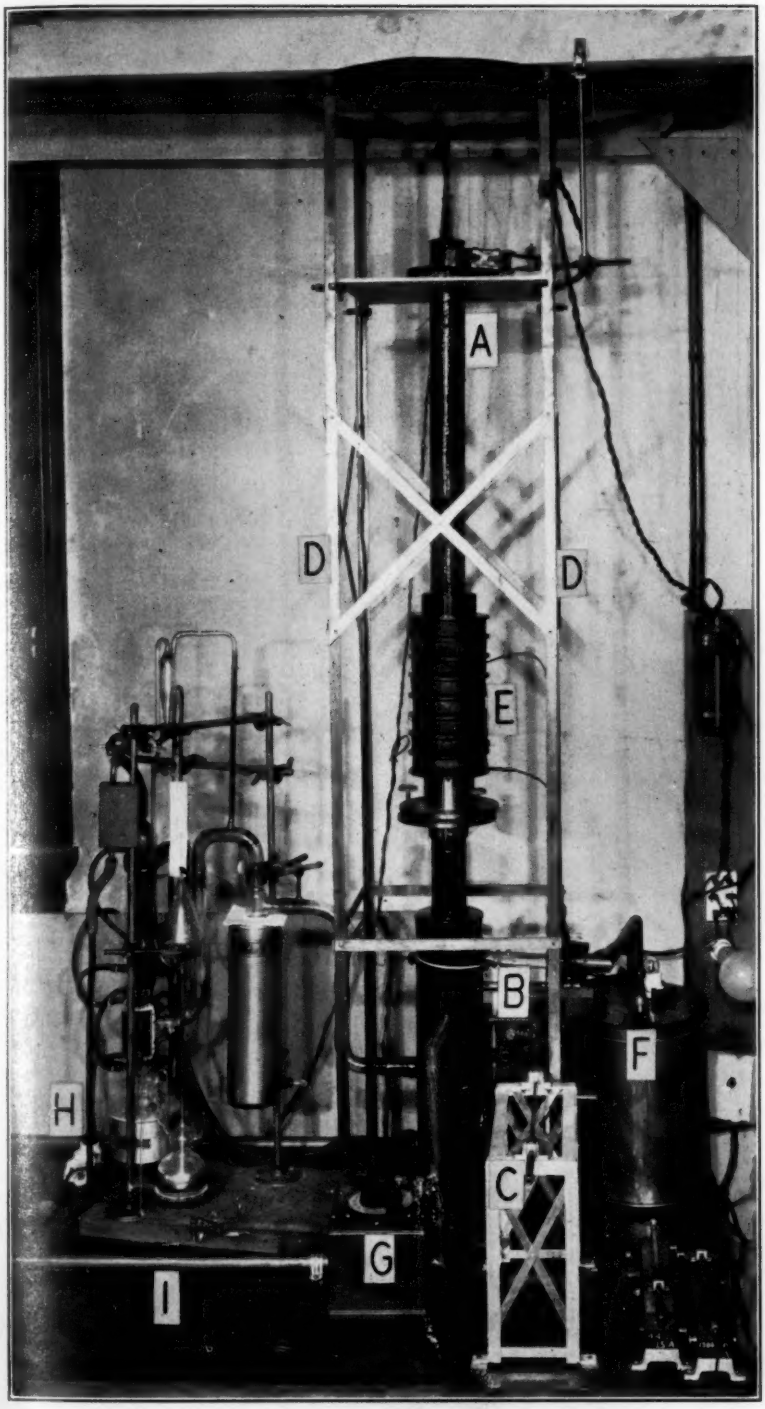

FIGURE 5.—*View of oscillograph and auxiliary apparatus.*

A, Oscillograph tube; B, camera; C, camera drive shaft; D, frame of compensating coils; E, focusing coil; F, capacitor (C_2 of figure 7); G, capacitor (C_4 of figure 7); H, shielded lead to specimen; I, shielded lead to air capacitor.

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The figure does not now close on itself and successive cycles are separated on the film as shown in the right-hand portion of figure 6. Sin α may still be approximated to a fair degree of accuracy from the

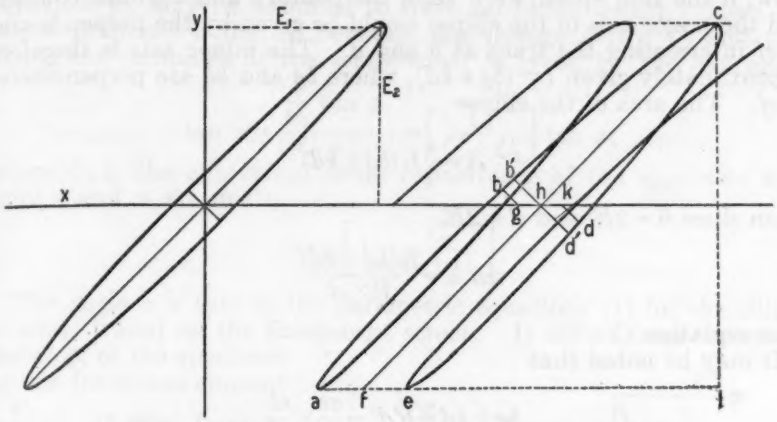

FIGURE 6.—*Measurement of power factor from oscillogram.*

following considerations: The film advances through a distance *ae* while a complete cycle is being traced. Starting from *a* the film has advanced one half of this distance when the tracing point reaches *c*.

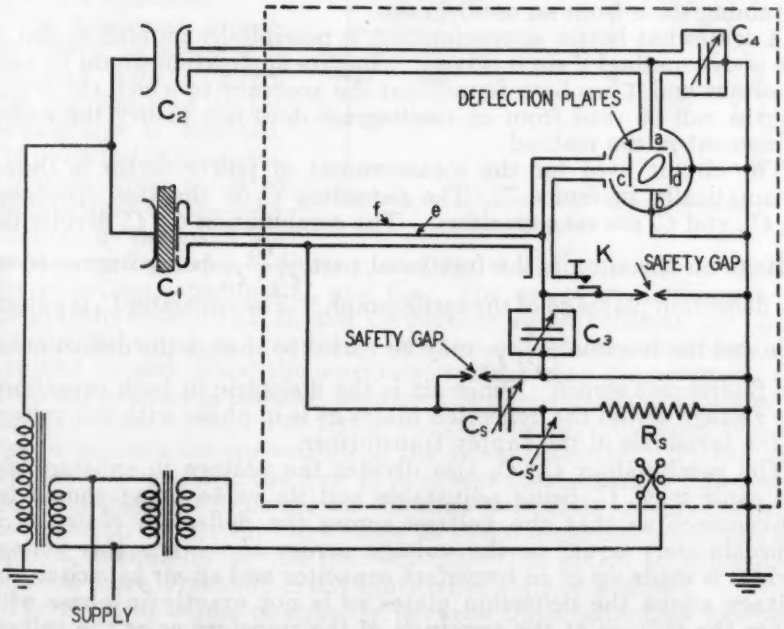

FIGURE 7.—*Details of electrical circuit used in measuring power factor.*

The points *a*, *c*, and *e* are fixed by the maximum displacements of the trace in the *y* direction. The *x*-axis bisects the perpendicular *cl* dropped from *c* to the line passing through *a* and *e*. The bisection of

ae determines *f*. The major axis of the ellipse is then approximately given by *cf*. From the intersection *h* of *cf* with the *x*-axis distances *gh* and *hk* along the axis are fixed each equal to one fourth of *ae*. Now, if the film speed were zero, the points *g* and *k* would coincide and the minor axis of the ellipse would be given by the perpendicular to *cf* intersecting the trace at *b* and *d*. The minor axis is therefore approximately given by $(bg+kd)$, where *bg* and *kd* are perpendicular to *cf*. The area of the ellipse

$$A=\frac{\pi}{4}fc(bg+kd)$$

Then since $fl=2E_1$ and $cl=2E_2$

$$\sin\alpha=\frac{fc(bg+kd)}{fl\times cl}$$

from equation (2).

It may be noted that

$$bg+kd=b'd'-\frac{ae}{2}\times\frac{cl}{cf}$$

Whence,

$$\sin\alpha=\frac{fc\times b'd'}{fl\times lc}-\frac{a\,e}{2fl}$$

The latter approximation is used as it reduces the labor involved in obtaining sin α from an oscillogram.

A somewhat better approximation is possible by an elaboration of the above method if sin α is large. But its application would be very laborious and it has been found that the accuracy to which the actual lengths can be read from an oscillogram does not justify the added refinement in the method.

The circuit used for the measurement of power factor is shown schematically in figure 7. The capacitor C_1 is the test specimen; C_2, C_3, and C_4 are air capacitors. The combination C_2, C_4 divides the voltage on the circuit, the fractional part $\frac{C_2}{C_2+C_4}$ being impressed on the deflection plates *ab* of the oscillograph. The capacitor C_4 is adjustable and the fraction $\frac{C_2}{C_2+C_4}$ may be varied to change the deflection on the fluorescent screen. Since air is the dielectric in both capacitors, the voltage across the deflection plates *ab* is in phase with the voltage at the terminals of the supply transformer.

The combination C_1, C_3 also divides the voltage in substantially the same way, C_3 being adjustable and its value being chosen for convenience so that the voltage across the deflection plates *cd* is approximately equal to the voltage across *ab*. Since this voltage divider is made up of an imperfect capacitor and an air capacitor, the voltage across the deflection plates *cd* is not exactly in phase with either the voltage at the terminals of the transformer or the voltage across the specimen as will be seen in figure 8. It can easily be shown, however, that the phase difference between the voltage across the deflection plates and the voltage at the terminals of the transformer differs by a small and computable amount from the phase defect of the specimen.

The phase-defect angle ϕ_1 of the specimen is defined as the complement of the angle between voltage and current and, for small angles, its value in radians is very nearly equal to the power factor. The air capacitor C_3 may be assumed to have no phase defect. Then the phase difference α (fig. 8) between the voltage across C_3 and that across the terminals of the transformer is given by the expression

$$\tan \alpha = \frac{\frac{1}{C_1}\tan \phi_1}{1/C_1 + 1/C_3} = \left[\frac{C_3}{C_1 + C_3}\right] \tan \phi_1$$

where C_1 is the equivalent series capacitance of the specimen and, since α and ϕ_1 are small,

$$\alpha \approx \phi_1 \left[1 - \frac{C_1}{C_1 + C_3}\right].$$

The angle α is that of the parametric equations (1) for the ellipse which is traced on the fluorescent screen. It differs from the phase defect ϕ_1 of the specimen by the fractional amount $\frac{C_1}{C_1 + C_3}$. If this fraction is kept small, then sin α as measured from the oscillogram may be regarded as the power factor of the specimen.

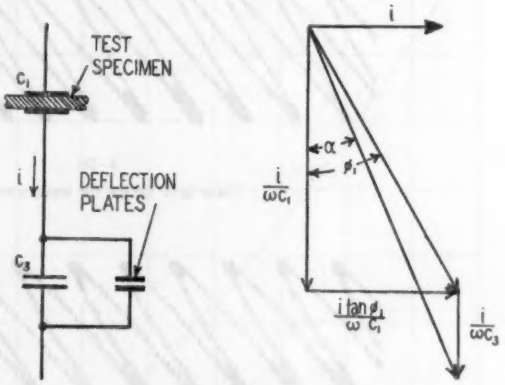

FIGURE 8.—*Current and voltage relations in measuring circuit.*

The specimen capacitor shown in figure 7 is equipped with a guard ring and the lead to the oscillograph is shielded. The potential of the shield f is maintained equal to the potential of the lead e from C_1 by means of the guard circuit shown. Adjustment of the shield potential is accomplished by the capacitors C_s and $C_{s'}$. The use of an auxiliary voltage in conjunction with R_s and $C_{s'}$ permits an adjustment for phase in the shield which is practically independent of the magnitude adjustment C_s and, since the auxiliary voltage may be reversed, the phase adjustment is possible whether the guard losses are greater or less than those in C_1. The figure on the oscillograph screen is itself used to indicate the correctness of the shield potential. To test this potential adjustment, the key K is closed momentarily, connecting the working circuit to its shield. If their potentials are not the same the ellipse on the screen will change its shape when the potentials are brought to equality by the short-circuit. The shield adjustment is correct if there is no shift of the figure when the key is closed.

The effect of a lack of equality between these potentials has been investigated and the analysis is presented in an appendix. It is shown that if the coupling capacitance between the measuring circuit and its shield is sufficiently small when compared to the capacitance in the measuring circuit, the effect of a small lack of adjustment of

shield potential is negligible. Hence the measuring circuit is not appreciably affected by local disturbances in the guard-ring capacitor even of the specimen is not uniform, and the power factor measured from oscillograms represents the losses in only the part of the specimen that is opposite the central measuring electrode.

IV. TESTS OF THE APPARATUS

Power factors obtained by the method described above have been compared with power factors measured on the same specimens under identical conditions with a Schering bridge. The bridge is of a completely shielded type similar to that described by Kouwenhoven and Baños.[10]

Measurements of power factor were made on specimens of varnished cambric and of micanite. The power factor of a sheet of varnished

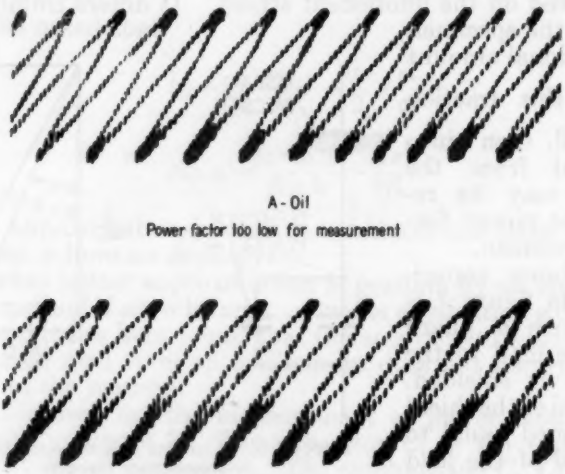

FIGURE 9.—*Typical oscillograms taken for low power factor materials.*

(Some retouching was necessary on the original oscillograms to improve the contrast in the figure.)

cambric was 0.0835 as measured on the Schering bridge. At the same voltage the power factor read from an oscillogram varied from 0.08 to 0.09 on four separate determinations, the average being 0.087. The power factor of a sheet of micanite was measured on the bridge as 0.033 while under the same conditions the power factor measured from oscillograms ranged from 0.033 to 0.045, the average of eight determinations being 0.039.

Figure 9 shows two oscillograms taken on transformer oil and micanite, respectively. The power factor of oscillogram *A* is too small for measurement. That of *B* is approximately 0.04. The difference in the type of figure is readily seen from inspection.

In order to test the set up at high power factors, sulfonated linseed oil was used as a dielectric. This oil has an abnormally high power

[10] Trans. A.I.E.E., vol. 51, p. 202, 1932. The bridge which was used differs from the one described by Kouwenhoven in the use of a mechanical rectifier and d-c galvanometer as detector. Furthermore, the detector shield is integral with the general shielding of the bridge instead of being connected to a branch point of the bridge itself.

factor at elevated temperatures. Two power-factor readings obtained with the bridge, with oil temperatures of 63 and 61 C and a stress of 100 volts per mil, were, respectively, 0.42 and 0.38. Between these two measurements an oscillogram was obtained at the same stress. This showed a power factor of 0.41. The oil had been heated previously and was cooling during the test.

The data given in the above comparisons are not the result of single measurements from individual cycles on the oscillogram, but are the averages of several readings on successive cycles.

In measuring power factors from the oscillograms the minor axis of the ellipse is the point of greatest uncertainty. When the figure is enlarged to a width of 5 cm, an error of 0.5 mm in the measure-

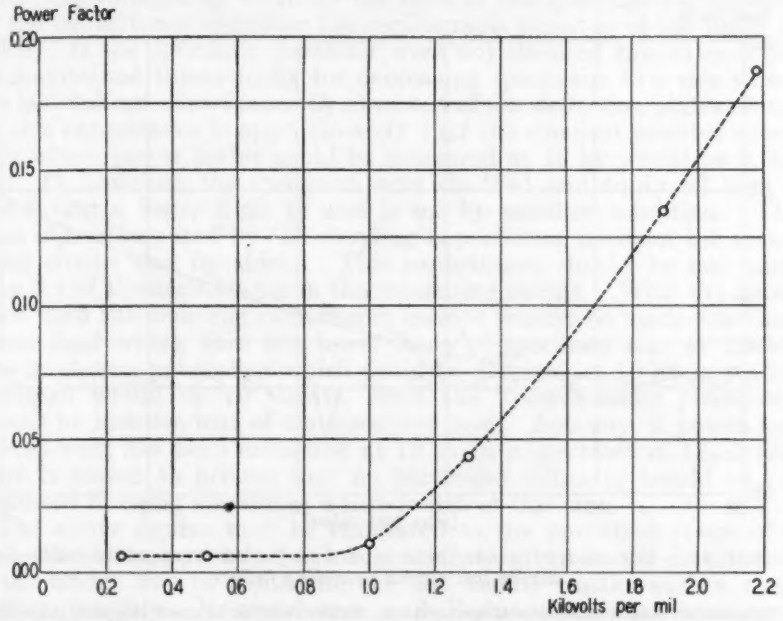

FIGURE 10.—*Variation of power factor with voltage for oil-impregnated cable paper.* Sample thickness was 5 mils.

ment of the minor axis amounts to about 0.02 in power factor. As errors of this magnitude are to be expected owing to inability to judge accurately the center of the trace on the oscillogram, we cannot hope to detect with certainty a power factor of much less than 0.02 and should expect individual measurements on any oscillogram to have a spread of about this amount.

To further examine the method a continuous record of power factor of a specimen of oil-impregnated cable paper was made with increasing voltage to the point of its electrical failure. The specimen had an area of about 50 cm^2 and a thickness of about 0.1 mm. It was oven-dried and impregnated in vacuum with oil at a pressure of about 1 mm Hg. After preliminary measurements of power factor at low stress with the Schering bridge, an oscillogram was recorded while the voltage was rapidly increased until the specimen failed. The results are shown in figure 10. The points recorded at 1,000

volts per mil and less represent values obtained with the Schering bridge. (These power factors are too small to read from the oscillogram.) Those above this value were taken from the oscillogram. The last plotted point is an average obtained from measurement on the last 5 cycles preceding breakdown. At this point the power loss in the specimen is of the order of 10 watts.

As a further illustration of the application of the method to the study of the electrical failure of insulation, data are taken from an investigation of this question which is now in progress. Figure 11 shows a cycle-by-cycle record of the power factor in two samples of impregnated 5-mil cable paper during the last second before its breakdown under electrical stress.[11] Curve *I* is plotted for a speci-

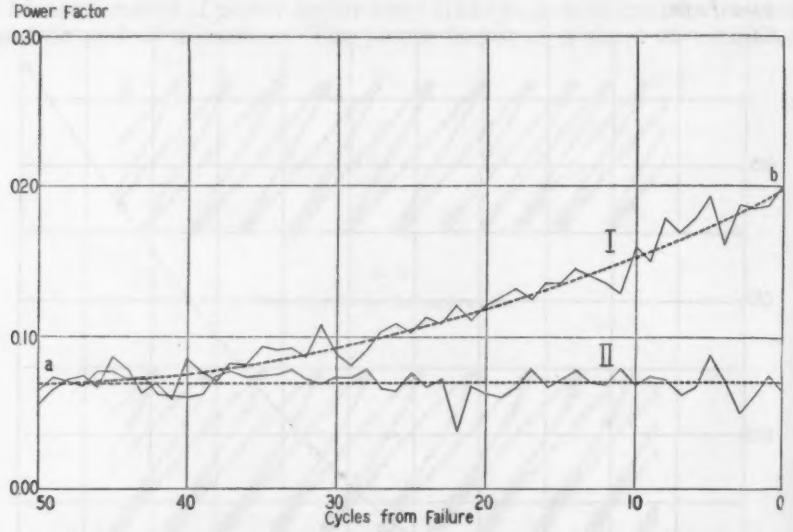

FIGURE 11.—*Variation of power factor with time for oil-impregnated cable paper during last second preceding failure.*

I. Failure occurred in working area of specimen. II. Failure occurred in guard ring area of specimen. Points connected by full line represent single readings in individual cycles and indicate the precision with which oscillograms may be read.

men which failed in the region covered by the central electrode. (See C_1, of fig. 7.) Curve *II* shows power factor in C_1 when the specimen failed in the guard ring capacitor. The plotted points represent single determinations from individual cycles of alternating stress and clearly show the order of precision with which such measurements can be made. At the point *a* of curve *I* the power loss in the specimen is 0.02 watt and at *b*, 0.1 watt. The central electrode used has an area of about 1 cm^2 and the capacitance of C_1 is 18$\mu\mu$f.

It should be noted that the disturbance in the guard circuit caused by approaching failure in the guard-ring capacitor (curve *II*) was not transmitted appreciably to the measuring circuit. This checks the results of the circuit analysis given in the appendix to this paper. The measuring circuit, as shown in the analysis, includes only the area of the specimen covered by the central electrode.

[11] This investigation is being carried on jointly with A. E. Peterson, to whom acknowledgment should be made for the use of the data.

V. CONCLUSION

It is apparent from the data given above that, while the method which has been described for measurement of power factor of dielectrics is quite limited as to the precision with which it will measure power factor itself, it is not nearly so restricted in the amounts of power which it will measure. The limit of precision in the measurement of power factor is set by the diameter of the tracing spot and by the size of the ellipse on the fluorescent screen of the oscillograph. The method is, however, well suited to the approximate determination of power factors over very short time intervals and is particularly adapted to the measurement of power factor in extremely small capacitors. At voltages up to 10 kv the ratio of the specimen capacitance to the capacitance shunting the oscillograph plates is of the order of 0.002. If the specimen capacitor were not shielded this ratio could be maintained theoretically for decreasing specimens to a size where the low-voltage capacitance C_3 consisted of the deflection plates alone. As this capacitance is approximately $1\mu\mu f$ the smallest possible specimen whose power factor could be measured at 10 kv would be 0.002 $\mu\mu f$. If, however, the specimen were shielded and equipped with a guard ring a lower limit to size is set by another condition. The limit is now imposed by the coupling capacitance between the measuring circuit and its shield. This capacitance should be not more than 0.1 of the capacitance in the measuring circuit. With the apparatus used the coupling capacitance cannot readily be made less than about $5\mu\mu f$ which fixes the lower limit of specimen size at $0.1\mu\mu f$. The minimum power loss which could be detected at 10 kv in such a specimen would be 10^{-4} watt, since the "power-factor precision" should be independent of the specimen size. Actually, a power loss of 0.02 watt has been measured at 10 kv in a specimen of $18\mu\mu f$ and there is reason to believe that no particular difficulty would be experienced in using specimens a hundredth of this size.

The above figures may be compared to the operating range of a high-sensitivity power-factor bridge. Data given in the description of the bridge due to Kouwenhoven and Baños [12] make such a comparison possible. Kouwenhoven and Baños state that specimens ranging in capacitance from $40\mu\mu f$ to $1{,}500\mu\mu f$ having power factors from 0.00007 to 0.16 have been measured in their bridge at 1.5 kv. Using the minimum values, their bridge can measure power loss of the order of 2×10^{-6} watt at 1.5 kv in a $40\mu\mu f$ specimen.

It will be seen that, although the precision of the above described oscillographic method for measuring power loss in dielectrics is low, its sensitivity is such that the losses in extremely small specimens can be approximately determined. This should make possible the examination of very minute volumes of an insulating material and the determination of highly localized losses in a nonuniform dielectric.

No limit can be fixed for the maximum specimen capacitance. This is determined solely by the amount of low-loss capacitance available for the capacitor which shunts the deflection plates of the oscillograph.

[12] See footnote 10, p. 96.

The author wishes to express his appreciation of the advice and suggestions of Profs. J. B. Whitehead and K. F. Herzfeld, of the Johns Hopkins University, under whose direction this work was initiated, and also his indebtedness to Prof. W. B. Kouwenhoven, of the same institution, for his suggestions.

VI. APPENDIX

The phase adjustment of the guard potential is made necessary by the difference in phase between C_1 and C_g of figure 12. The capacitor C_g includes not only the guard ring itself (see fig. 7), but

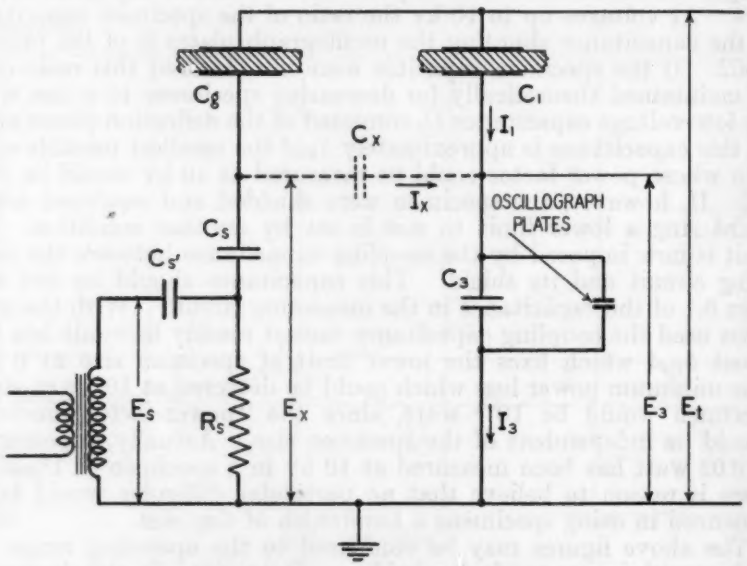

FIGURE 12.—*Details of circuit used in shielding.*

also the supporting framework which holds the electrode assembly. The phase defect of C_g therefore is a result of losses in all of the insulation that goes to make it up including the guard-ring portion of the specimen under observation with its edge effects, the insulating supports of the electrode assembly and portions of the vessel in which the assembly is mounted.

The phase difference between E_x and E_3 of figure 12 is in general such that it cannot be eliminated simply by the use of a variable resistance in series with C_3. The quadrature voltage inserted in this way may be 180 degrees out of phase with that necessary to correct the shield potential. The use of an auxiliary voltage introduced into the shield circuit by means of a transformer makes it possible to obtain the necessary 180° shift in the quadrature voltage. Since the voltage supply of this transformer is the same as that of the high-voltage transformer used to supply E_t, E_s will be a constant fraction of E_t. The fraction of E_s which is inserted into the shield circuit as a quadrature voltage across R_s may be adjusted by changing

the value of the capacitor $C_{s'}$. The in-phase component of E_x may be independently adjusted by the variable capacitor C_s. The shield potential E_x should then remain equal to the working potential E_3 when the voltage E_t on the specimen is altered.

If, however, the specimen of insulation under examination is not uniform, losses may not increase at the same rate in the working capacitor C_1 and in the guard-ring capacitor C_g, particularly in the region of instability which precedes the failure of the specimen. When this occures the potentials of the working circuit and of the shield will no longer be equal and the capacitance between them will tend either to feed current into the measuring circuit or draw it off, depending on the direction of the potential inequality. It is, therefore, necessary to consider the interaction between the measuring circuit and its shield caused by their capacitive coupling.

The network to be considered is shown in figure 12. The following vector relations are apparent:

$$E_x = \rho E_t \tag{1}$$

ρ being a complex quantity which takes into account the ratio of E_x and E_t and also their phase relation.

$$E_3 = \frac{I_3}{j\omega C_3} \tag{2}$$

where C_3 includes the capacitance of the oscillograph plates.

$$I_x = (E_x - E_3) j\omega C_x \tag{3}$$

$$I_1 = (E_t - E_3) j\omega\gamma C_1 \tag{4}$$

where $\gamma = \cos\ \phi_1(\cos\ \phi_1 - j\ \sin\ \phi_1)$; ϕ_1 being the phase defect of C_1. Here C_1 is the equivalent series capacitance of the specimen.

$$\begin{aligned} I_3 &= I_1 + I_x \\ &= (E_x - E_3) j\omega C_x + (E_t - E_3) j\omega\gamma C_1 \end{aligned} \tag{5}$$

From (2) and (5) we have

$$E_3 = \frac{1}{j\omega C_3}\left[(E_x - E_3)\, j\omega C_x + (E_t - E_3)\, j\omega\gamma C_1\right]$$

whence

$$\begin{aligned} E_3\left(1 + \frac{C_x}{C_3} + \gamma\frac{C_1}{C_3}\right) &= \frac{1}{C_3}[E_x C_x + \gamma E_t C_1] \\ &= \frac{E_t}{C_3}[\gamma C_1 + \rho C_x] \end{aligned}$$

or

$$\frac{E_3}{E_t} = \frac{\gamma C_1 + \rho C_x}{C_3 + C_x + \gamma C_1} \tag{6}$$

and

$$\frac{E_3}{E_x} = \frac{E_3}{\rho E_t} = \frac{\dfrac{\gamma C_1}{\rho} + C_x}{C_3 + C_x + \gamma C_1} \tag{7}$$

Now let $\dfrac{E_3}{E_x} = 1 + k$ where k is the fractional departure of the shield potential from that of the working circuit.

Then from (7)

$$1+k=\frac{\frac{\gamma C_1}{\rho}+C_x}{C_3+C_x+\gamma C_1}$$

and

$$\rho=\frac{\gamma C_1}{C_3+\gamma C_1+k(C_3+C_x+\gamma C_1)} \tag{8}$$

Substituting (8) in (6)

$$\frac{E_3}{E_t}=\frac{\gamma C_1\left[1+\frac{C_x}{C_3+\gamma C_1+k(C_3+C_x+\gamma C_1)}\right]}{C_3+C_x+\gamma C_1}$$

$$=\frac{\frac{\gamma C_1}{C_3+\gamma C_1}\left[1+\frac{C_x}{C_3+\gamma C_1}\left\{\frac{1}{1+k\left(1+\frac{C_x}{C_3+\gamma C_1}\right)}\right\}\right]}{1+\frac{C_x}{C_3+\gamma C_1}}$$

$$=\frac{\gamma C_1}{C_3+\gamma C_1}\left[1-k\frac{C_x}{C_3+\gamma C_1}\left\{1-k\left(1+\frac{C_x}{C_3+\gamma C_1}\right)+k^2\left(1+\frac{C_x}{C_3+\gamma C_1}\right)^2\cdots\right\}\right]$$

The voltage division to be expected in the measuring circuit if the shield potential is correct is

$$\frac{E_3}{E_t}=\frac{\gamma C_1}{C_3+\gamma C_1}$$

If the shield potential is unbalanced by a fractional amount, k, then the measuring circuit is changed (to a first approximation) by a fraction $k\frac{C_x}{C_3+\gamma C_1}$. This will be negligible if $\frac{C_x}{C_3+\gamma C_1}$ is kept small. In the apparatus used this ratio is less than 0.04 and it is believed that the power factor measured for the specimen C_1 is quite independent of local disturbances in the part of the specimen which forms the dielectric of the guard-ring capacitor C_g.

WASHINGTON, June 1933.

U.S. DEPARTMENT OF COMMERCE BUREAU OF STANDARDS

RESEARCH PAPER RP637

Part of Bureau of Standards Journal of Research, vol. 12, January 1934

INFLUENCE OF NEIGHBORING STRUCTURES ON THE WIND PRESSURE ON TALL BUILDINGS

By C. L. Harris [1]

ABSTRACT

Measurements have been made of the wind pressure over a model of the Empire State Building as affected by the presence of neighboring models simulating buildings which might be erected on the adjacent blocks. The object was to determine the shielding effect for different directions of the wind.

While the pressure on certain faces of the building was increased somewhat by the presence of the neighboring structures, the resultant of pressure on the windward face and suction on the lee face was decreased. The decrease was greatest when the interfering structure was close by and directly upstream. The height shielded was not so great as the height of the interfering structure.

Shielding may produce a variation in the twisting moment about a vertical axis at different levels. The stresses set up by this loading may require consideration in special cases.

CONTENTS

	Page
I. Introduction	103
II. Measurements of wind pressure	104
1. Apparatus	104
2. Method of presenting data	105
3. Results	107
III. Analysis of the results with reference to the design of tall buildings	117

I. INTRODUCTION

One of the most important problems, from a structural standpoint, in the design of a tall building is the wind-bracing system. Experiment as well as theory is required as a guide in the designing of the various members and their connections of a structure that is to be both safe and rigid.

Just what wind pressure a building may have to withstand, no one knows. The wind pressure depends in the first instance on the maximum wind velocity encountered. Much valuable information on the maximum wind velocities observed in different parts of the country is published yearly by the United States Weather Bureau in Washington, and these data should be consulted when a tall building is to be designed. The main Committee for Standardization of Building Codes in the Netherlands [2] recommends that the pressure

[1] Professor of architectural engineering, and head, department of architecture, the Pennsylvania State College, State College, Pa. The measurements described in this paper were made during a year's leave of absence from the college and as guest at the Bureau of Standards. A further account is given in Technical Bulletin No. 18, School of Engineering, Pennsylvania State College.

[2] Het Bouwbedrijf, Aug. 26, 1932, and Oct. 21, 1932. Wind-belasting op Bouwerken, by R. L. A. Shoemaker and I. Wouters.

to be used in the design of buildings shall vary with the locality in which the building is to be erected. A chart has been made showing what maximum wind velocities may be expected in any part of the Netherlands.

The wind pressure also depends on the shape of the structure and on its exposure. Although the individual factors are not separately discussed, the building codes of some of the larger cities modify the requirements to satisfy surrounding conditions of exposure and protection. In some instances there is a variation according to height (reflecting the change of wind velocity with height), while in others a certain constant pressure is to be used above a given distance from the ground. The building ordinance of Amsterdam (Netherlands) provides for a wind pressure of 21 to 51 lb per sq. ft. according to exposure. The Prussian regulations provide for a variation of 15 to 45 lb per sq. ft. depending upon the height, exposure, and location of the building. At a recent meeting of the structural division of the American Society of Civil Engineers [3] it was recommended that the wind pressure to be finally adopted in any case should be based not only on information furnished by observation stations situated in the locality concerned, but also on such other factors as shielding and the effects of turbulence. The belief still exists that 20 lbs. per sq. ft for the first 500 ft, increased by 2 lb per sq ft for each additional 100 ft, is generally adequate for purposes of design.

The relation between wind pressure and wind speed has been most often studied by wind-tunnel experiments on models.[4] A recent investigation of the wind pressure on a model of the Empire State Building in the 10-foot wind tunnel at the Bureau of Standards [5] showed that for this building the pressure was $0.0038V^2$ lb per sq ft where V is the wind speed in mph.

It is the purpose of this paper to show how the distribution of pressure on the same building would be affected by the existence of nearby buildings, using models to simulate certain specified conditions.

II. MEASUREMENTS OF WIND PRESSURE

1. APPARATUS

The model of the Empire State Building and the method of making measurements of wind pressure have been fully described in Research Paper No. 545. Figure 1 is a photograph of that and the other two models used in the present study. They were mounted in the 10-foot wind tunnel of the Bureau of Standards on a platform simulating the ground. The three models are designated A, B, and C, and are shown in their relative positions in figure 3. The model of the Empire State Building (model A) and the distances between the models are to a scale of 1 to 250 and represent a possible future condition at the intersection of Fifth Avenue and Thirty-third Street in New York City.

[3] Civil Engineering, March 1933.

[4] For a full discussion of the use of models and the principles of similitude, refer to: Osborne Reynolds, Scientific Papers, vol. 2, paper no. 61, p. 524; Prof. Stokes, On the Effect of Internal Friction on the Motion of the Pendulum, Trans. Cambridge Phil. Soc. 1851-56; Alton C. Chick and John R. Freeman, Dimensional Analysis and The Principle of Similitude as Applied to Hydraulic Experiments with Models, A.S.M.E. Proceedings, 1929; E. Buckingham, Model Experiments and the Forms of Empirical Equations, A.S.M.E. Spring Meeting, 1915; Benj. Groat, Trans. A.S.M.E. vol. 96.

[5] H. L. Dryden and G. C. Hill, B.S. Jour. Research, vol. 10. (RP 545), April 1933.

Model *A* was made of aluminum, models *B* and *C* of wood finished to a smooth surface. All three models were mounted on a circular plate which in turn was placed on a platform, the front edge of which was brought to a knife-edge thickness. The whole group was arranged so that the top of model *A* and the platform were equidistant from the tunnel axis. By means of ball bearings under the circular plate the entire group could be rotated through 360°, so that observations could be made for any desired direction of wind relative to the group. When face *D* (fig. 3) of model *A* was set normal to the direction of the wind, the direction was called 0°. This corresponds to the wind blowing up Fifth Avenue. Angles increase as the plate is rotated clockwise. Readings were taken at angles of 0°, 20°, 40°, 50°, 70°, and at angles 90°, 180°, and 270° greater than each of these, but only certain of these at 40°, 160°, and the pairs 0°, 180°, and 90°, 270° are discussed in this paper.

Only model *A* had pressure holes, or observation stations. There were 17 holes at each of the 3 levels corresponding to the seventy-fifth, fifty-fifth, and thirty-sixth floors of the actual building, these levels being denominated *A*, *B*, and *C*, respectively (figs. 1 and 2). The pressure holes were mainly on two faces of the model, so that it was necessary to rotate model *A* through 180° with respect to the other models in order to make observations at all angles.

Model *B* represents a building 640 feet high facing the Empire State Building on Fifth Avenue and extending back along Thirty-third and Thirty-fourth Streets about 200 feet. The setbacks and size of tower are, with some slight modifications, in accordance with the recommendations of the Regional Plan of New York and Its Environs.[6]

The setbacks of model *C* along Fifth Avenue are the same as those of the Empire State Building, and the top of *C* is at the height of the middle line of pressure holes in *A* (figs. 1 and 3). The first makes it possible to study the effect, if any, on the pressure on face *A*, model *A*, when the wind is parallel to that face, and the corresponding face of the screening object (*C*) is, at every level, in the same plane as face *A*, model *A*. The second was for the purpose of determining whether the shielding effect extended to the full height of the interfering structure.

2. METHOD OF PRESENTING DATA

When the air is at rest, as we experience it in a room with all openings closed, or in a calm, the pressure exerted by it is of equal intensity in all directions. When the air has been set in motion, an object moving with the speed and in the direction of the wind is also subject to a uniform distribution of pressure. The magnitude of this pressure is called the static pressure, or the normal atmospheric pressure. When there is a relative motion between the object and the air, the intensity of pressure is changed. The change may be either an increase or a decrease with respect to the static pressure, depending upon the direction of the wind with respect to some reference line fixed in the object. In general, it may be said that the air pressure on objects exposed to the wind will be increased on the windward side and decreased on the leeward side. At some points there will be no change from the static pressure.

[6] Thomas Adams, Limiting the Size of Buildings, Civil Engineering, October 1932.

Thus when the wind blows against a surface, p, the force per unit of area at any point may be regarded as consisting of two parts—the static pressure p_s and the increase, or wind pressure, p_w, which

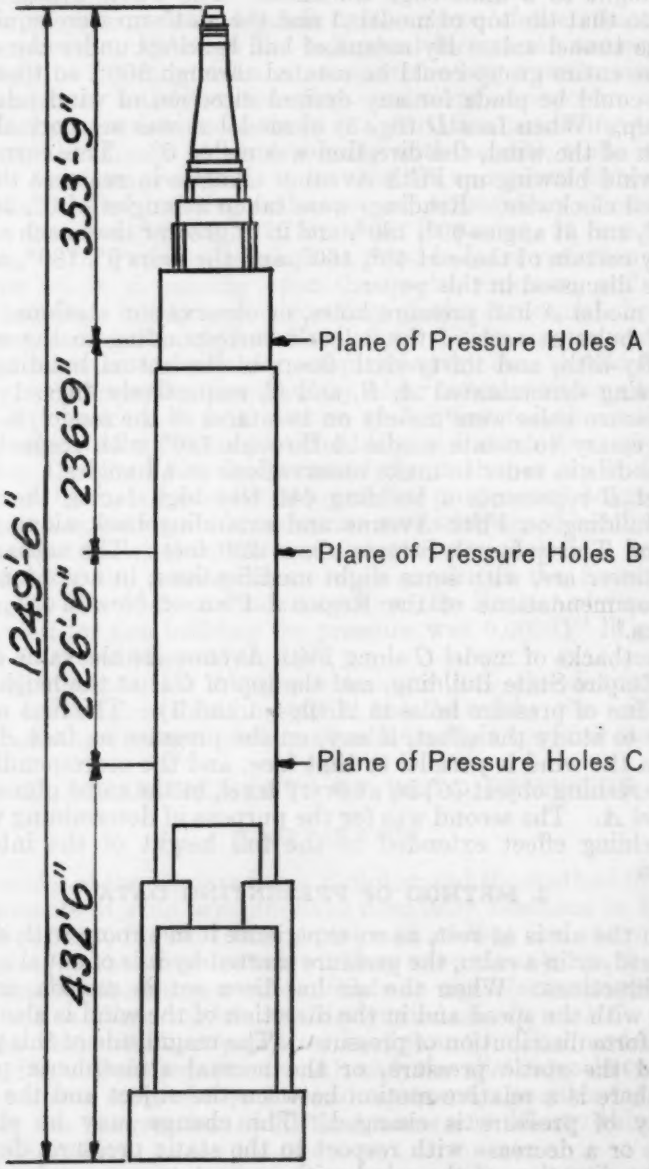

FIGURE 2.—*Location of sections A, B, and C on the Empire State Building.*

equals $p-p_s$. The wind pressure may be either positive or negative or zero. The maximum possible increase in pressure due to the wind is called the velocity pressure and is $q=\frac{1}{2}\rho V^2$, where ρ is the density of the air, and V the velocity of the wind.

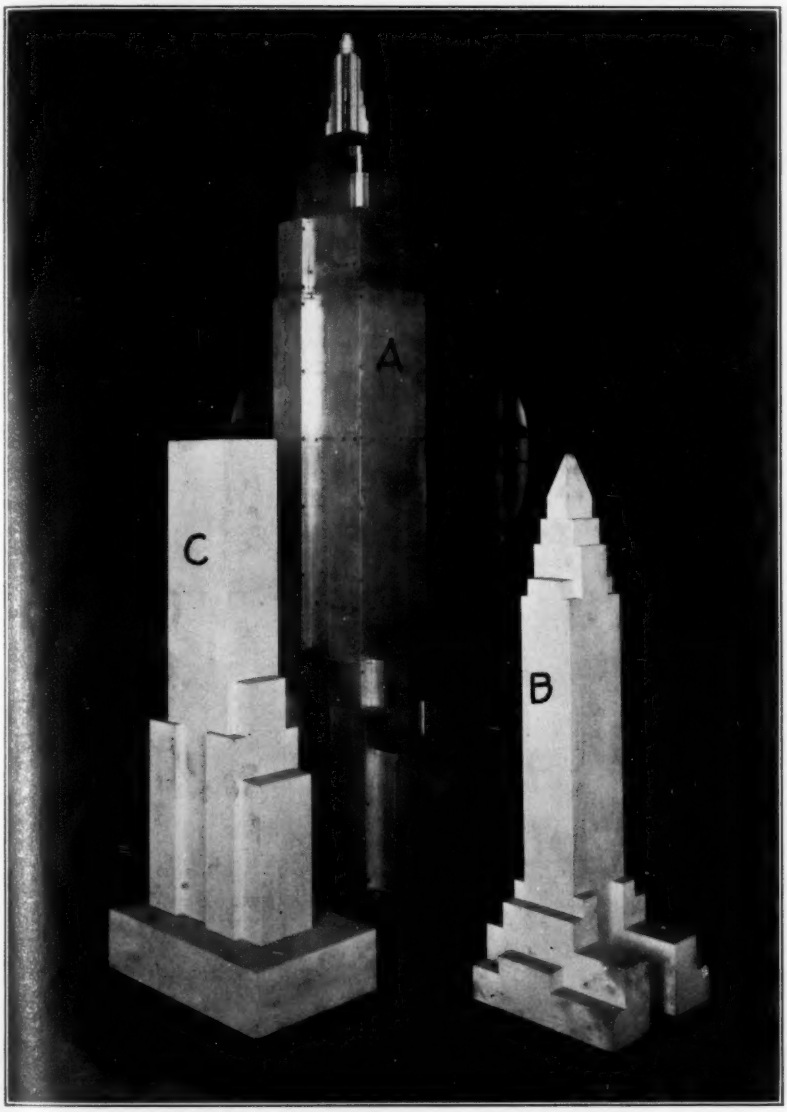

FIGURE 1.—*Models mounted on platform in the wind tunnel.*

The pressure holes are drilled in brass plugs which appear as dark spots at 3 levels. The other dark spots are brass screws holding the model together.

UNIV. OF MICH.

It is customary in aerodynamic work to measure the wind pressure in terms of the velocity pressure q, to express the results in terms of the coefficient p_w/q. The coefficients thus obtained are independent of the units of measurement so long as the units used are consistent, and in many cases are independent of both the wind speed and the size of the model; in such cases data obtained from the model may be applied directly to the prototype. When the ratio of the wind pressure to the velocity pressure is not a constant we have what is called a scale effect. The pressure coefficient is then a function of the Reynolds number, $\frac{VL\rho}{\mu}$ where L is a dimemsion fixing the scale, and μ is the viscosity of the air; and unless the scale effect is small it is difficult to infer from the observations the pressures to which the prototype will be subjected at a given wind velocity. Usually, however, the scale effect is small, the average value of the pressure coefficient differing from its extremes by only 2 or 3 percent, which is well within the factor of safety used in design.

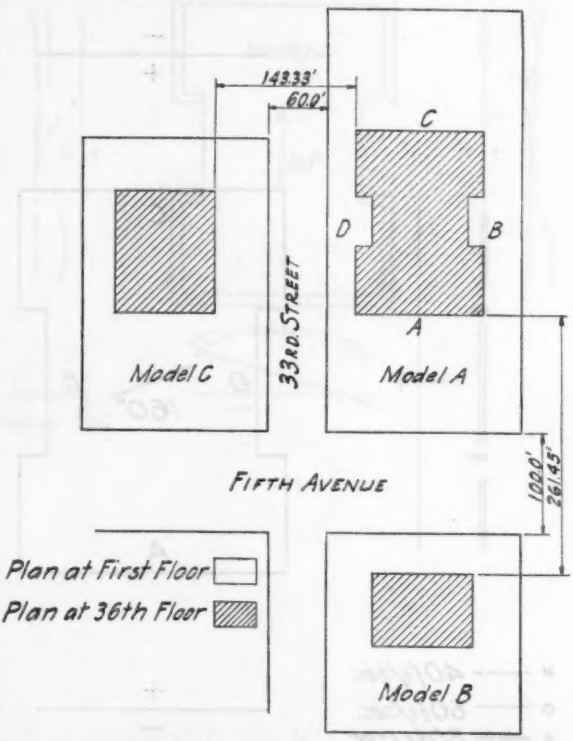

FIGURE 3.—*Plan, to scale, of assumed location which was reproduced on a scale of 1:250 on the platform in the wind tunnel.*

3. RESULTS

In this investigation, measurements were made at three wind speeds, 40, 60, and 80 ft/sec. The pressure coefficients p_w/q for each speed were computed as explained in Research Paper 545.

It was observed in a number of instances that the pressure coefficient varied systematically when the speed was changed; in other words, there was some scale effect. No broad statement can be made that applies to all stations and directions of the wind; in general, the pressures tend to be somewhat greater at the higher speeds, and in few instances does the extreme difference exceed $0.1q$. For about 40 percent of the total number of observations, the individual readings did not depart from the mean by more than $0.02q$.

As an illustration of the magnitude of the scale effect found, consider the observations at section A, well above levels B and C, with wind at 160° (fig. 4). It will be observed that the pressure distribution curves for the three speeds resemble each other very closely. Some of the differences shown are due not to variations in scale effect, but to unavoidable limitations in the precision of the measurements. Although there is somewhat greater evidence of scale effect than in the similar measurements given in Research Paper 545 for model A alone, it is still so small that it is considered negligible for

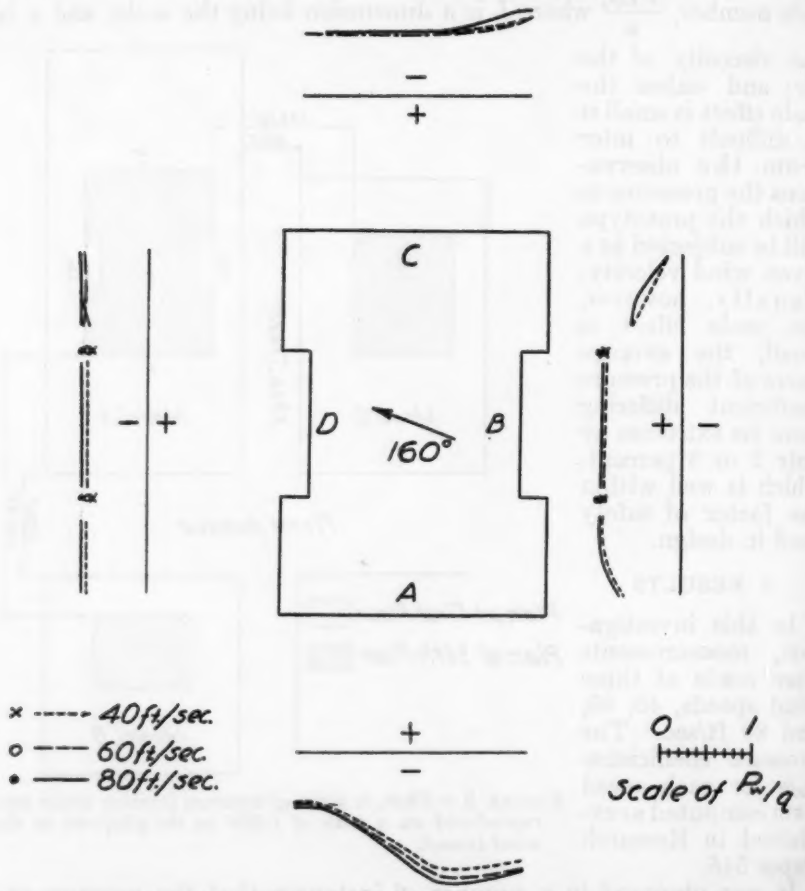

FIGURE 4.—*Distribution of pressure at section A for the speeds indicated, setting 160°. Wind in direction of arrow.*

purposes of design. Consequently, it has been ignored in the cases now to be considered, and the slightly differing coefficients corresponding to the several wind velocities have been averaged. The average alone is given and discussed.

The effect of the presence of the neighboring models B and C on the pressure on model A is indicated by the change in the distribution of the pressure over A when the direction of the wind is changed by 180°; an obstruction that is on the lee side of A for one of those directions will be on the windward for the other. Data for forces

normal to the wind directions are given in table 1 (page 112) for two such pairs of wind directions.

For wind along Fifth Avenue, directions 0° and 180°, the change in the average pressure coefficient on going from 180° (*C* to lee) to 0° (*C* to windward) was for the windward face of *A:* An

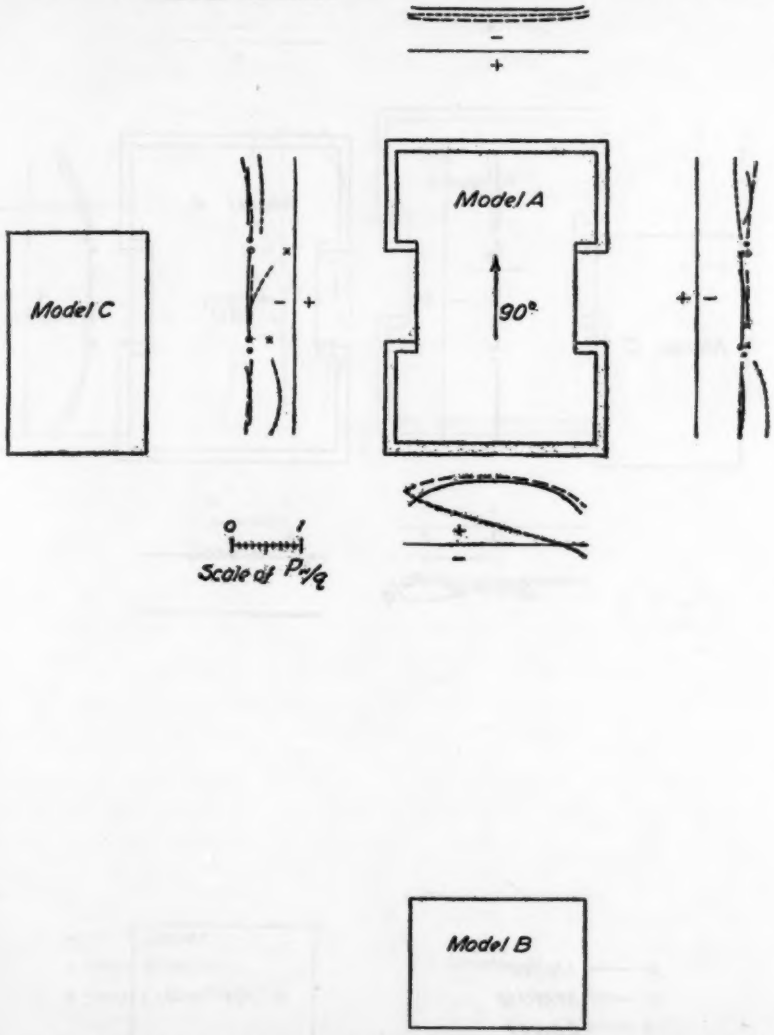

FIGURE 5.—*Distribution of pressure for setting 90°. Wind in direction of arrow.*

The pressures are measured from the static pressure (in the absence of all models) as base and expressed as ratios to the velocity pressure. Positive ratios are plotted inward from the thin base lines to the scale shown. Minus signs denote that the pressure is lower than the static pressure. The circles and crosses give the values at stations 10, 14, 27, and 31 on the side walls of the embrasures. (See figs. 9, 10, 11.)

increase from 0.71 to 0.79, or 11 percent at the upper row of holes; at the middle row, a decrease of 7 percent; and at the lower row a decrease from 0.77 to −0.54, or 170 percent. For the same change in the wind (180° to 0°) the change in the suction (negative-pressure

coefficient) on the lee face of A was: A decrease of 21 percent at the upper row, of 14 percent at the middle row, and an increase of 7 percent at the lower row. The combined effect of pressure on the wind-

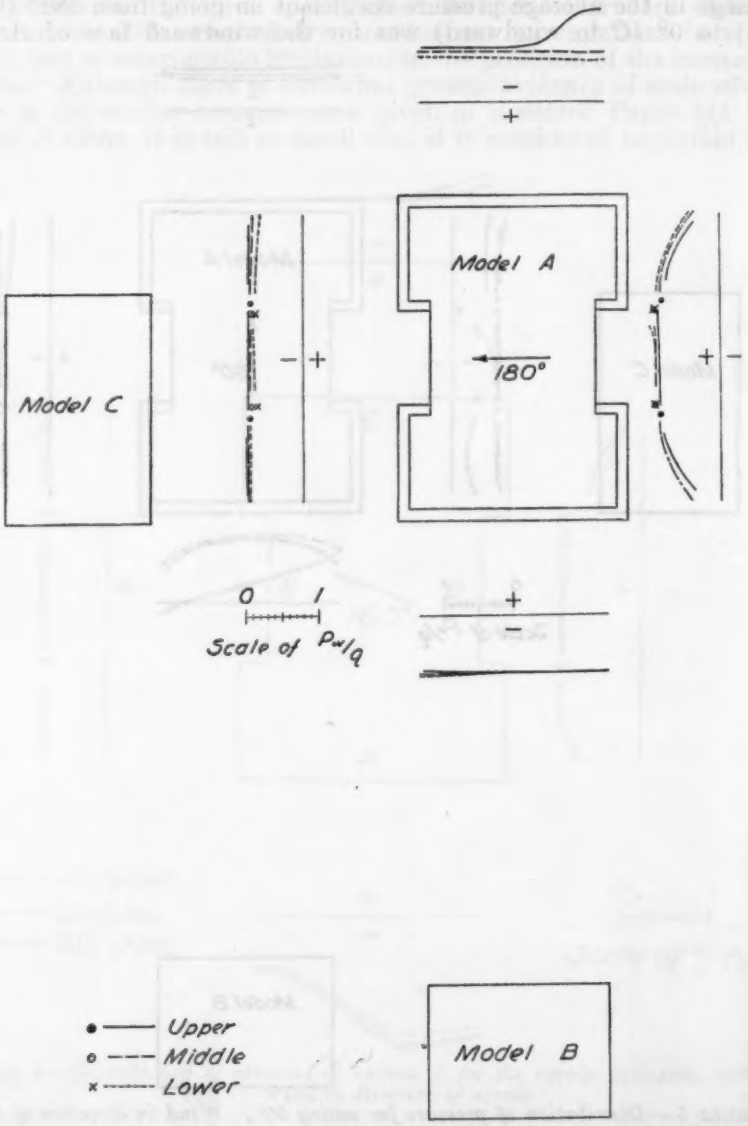

FIGURE 6.—*Distribution of pressure for setting 180°. Wind in direction of arrow.*

The pressures are measured from the static pressure (in the absence of all models) as base and expressed as ratios to the velocity pressure. Positive ratios are plotted inward from the thin base lines to the scale shown. Minus signs denote that the pressure is lower than the static pressure. The circles and crosses give the values at stations 10, 14, 27, and 31 on the side walls of the embrasures. (See figs. 9, 10, 11.)

ward face and suction on the lee face decreases by 6, 11, and 87 percent at the upper, middle, and lower row of holes when the wind changes from 180° to 0°. The distribution of pressure in these cases is shown in figures 6 and 7.

Similarly for wind along Thirty-third Street. When the wind changes from 270° (*B* to lee) to 90° (*B* to windward) the average pressure coefficient for the three rows of holes in the order upper,

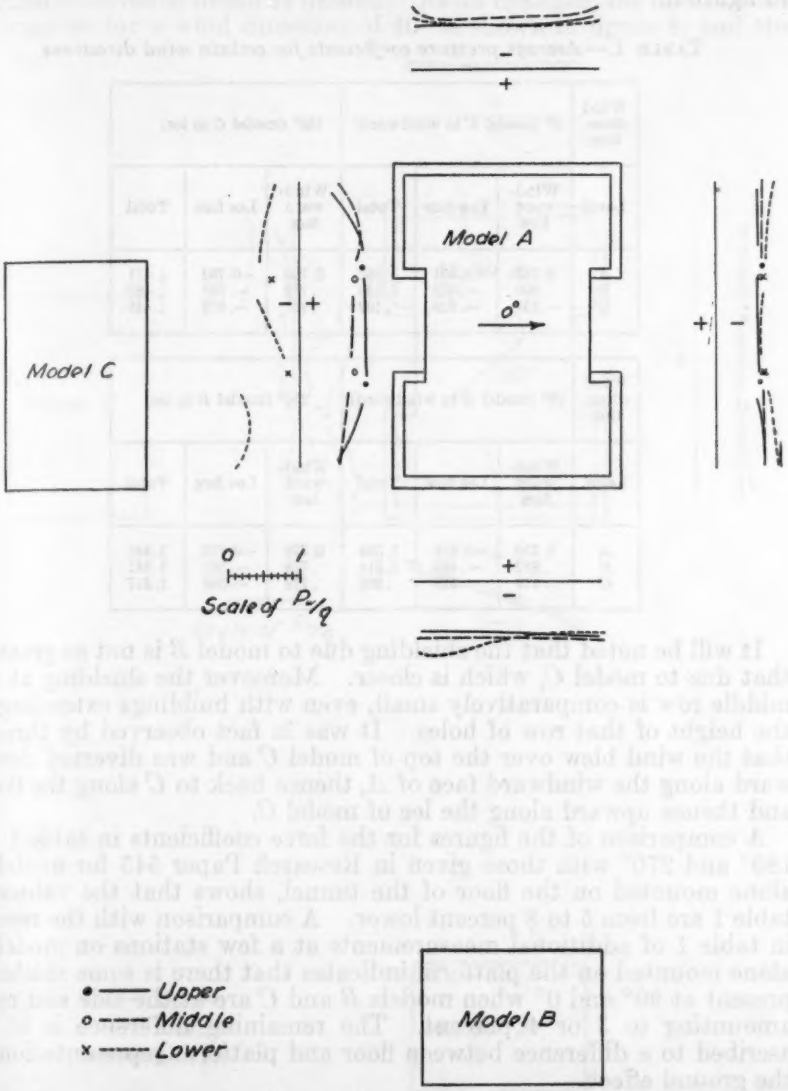

FIGURE 7.—*Distribution of pressure for setting 0°. Wind in direction of arrow.*

The pressures are measured from the static pressure (in the absence of all models) as base and expressed as ratios to the velocity pressure. Positive ratios are plotted inward from the thin base lines to the scale shown. Minus signs denote that the pressure is lower than the static pressure. The circles and crosses give the values at stations 10, 14, 27, and 31 on the side walls of the embrasures. (See figs. 9, 10, 11.)

middle, and lower on the windward face of *A* increases by 4 percent, increases by 7 percent, and decreases by 64 percent; and the suction (negative coefficient) for the holes on the lee face of *A* decreases by

15 percent, by 14 percent, and by 2 percent. The combined effect of pressure and suction decreases by 6 percent, by 2 percent, and by 39 percent. The distribution of pressure for the 90° direction is shown in figure 5.

TABLE 1.—*Average pressure coefficients for certain wind directions*

Wind direction	0° (model *C* to windward)			180° (model *C* to lee)		
Level	Windward face	Lee face	Total	Windward face	Lee face	Total
A	0.785	−0.601	1.386	0.709	−0.762	1.471
B	.699	−.633	1.332	.752	−.737	1.489
C	−.537	−.729	.192	.767	−.679	1.446

Wind direction	90° (model *B* to windward)			270° (model *B* to lee)		
Level	Windward face	Lee face	Total	Windward face	Lee face	Total
A	0.750	−0.616	1.366	0.724	−0.722	1.446
B	.832	−.482	1.314	.778	−.563	1.341
C	.279	−.529	.808	.779	−.538	1.317

It will be noted that the shielding due to model *B* is not as great as that due to model *C*, which is closer. Moreover the shielding at the middle row is comparatively small, even with buildings extending to the height of that row of holes. It was in fact observed by threads that the wind blew over the top of model *C* and was diverted downward along the windward face of *A*, thence back to *C* along the floor, and thence upward along the lee of model *C*.

A comparison of the figures for the force coefficients in table 1 for 180° and 270° with those given in Research Paper 545 for model *A* alone mounted on the floor of the tunnel, shows that the values in table 1 are from 5 to 8 percent lower. A comparison with the results in table 1 of additional measurements at a few stations on model *A* alone mounted on the platform indicates that there is some shielding present at 90° and 0° when models *B* and *C* are at the side and rear, amounting to 3 or 4 percent. The remaining difference is to be ascribed to a difference between floor and platform representation of the ground effect.

It should be noted here that the changes in the average coefficients for the separate faces are of limited significance, since the base pressure is taken more or less arbitrarily as the static pressure when no buildings are present. A change in the base pressure would affect the forces on the separate faces, although the sum of the effects on the windward and lee faces would be unchanged. In an actual building, the interior pressure is not necessarily equal to the static pressure used as the base pressure from which other pressures are measured in the model experiments. Hence the loadings on individual wall panels or faces of the building may differ by a uniformly distributed loading

from that tabulated. The value of the interior pressure does not, however, affect the total forces and moments on the building.

From the data obtained, the loading on the building may be studied in as much detail as desired. As an example, the distribution of pressure for a wind direction of 40° is shown in figure 8, and the

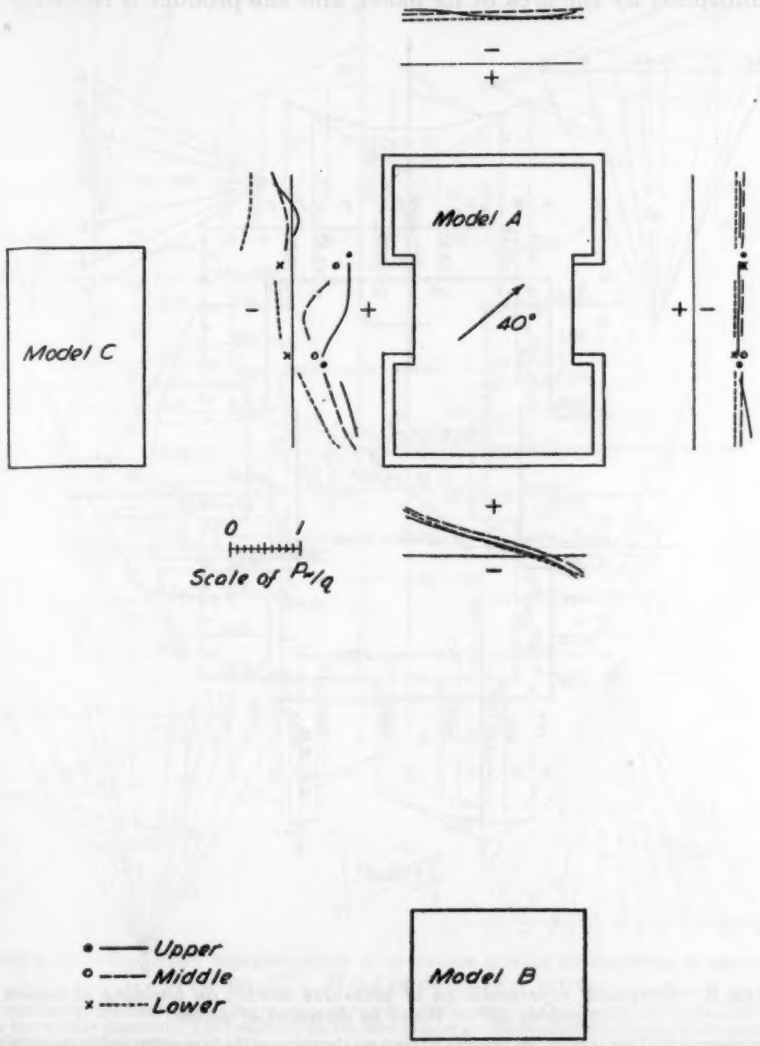

FIGURE 8.—*Distribution of pressure for setting 40°. Wind in direction of arrow.*

The pressures are measured from the static pressure (in the absence of all models) as base and expressed as ratios to the velocity pressure. Positive ratios are plotted inward from the thin base lines to the scale shown. Minus signs denote that the pressure is lower than the static pressure. The circles and crosses give the values at stations 10, 14, 27, and 31 on the side walls of the embrasures. (See figs. 9, 10, 11.)

resultant loading is analyzed for the three levels in figures 9, 10, and 11. The diagrams in these figures are force diagrams for the full scale building.

The procedure by which the several pressure coefficients were combined in obtaining the total force is this. Imagine a strip 1 foot wide

taken around the entire building, the center of its width coinciding with the line of pressure holes. On each face of the building draw vertical lines midway between the holes. These lines together with the edges of the faces divide the strip into a series of panels, in each of which is a single pressure hole. The pressure coefficient for each hole is multiplied by the area of its panel, and the product is regarded as

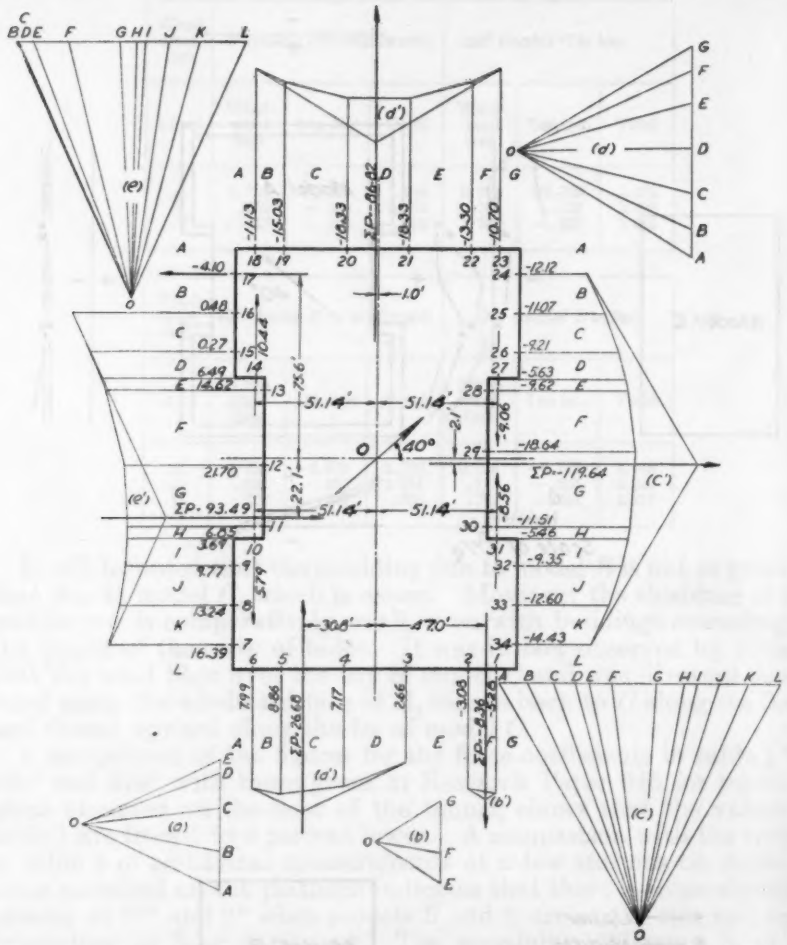

FIGURE 9.—*Graphical representation of pressures exerted on building at section A at setting 40°. Wind in direction of arrow.*

The numbers on the lines through the pressure stations are the values of the force acting on the panel divided by the velocity pressure. The resultants on the several faces are determined graphically in the auxiliary diagrams, *a*, *a'*, *b*, *b'*, etc.

the ratio of the actual force on that panel to the velocity pressure q. Although the holes are not in all cases at the centers of their respective panels, the error so caused is small.

These products are entered along lines through the pressure stations perpendicular to the faces. The resultant forces and the lines of application of the resultants on each face have been constructed graphically. Where positive and negative values are found on the same face, the resultant is given for each separately.

It is evident that when the wind pressure in a given horizontal plane is unevenly distributed on the sides of a building there is produced a torsional effect about a vertical axis in addition to the overturning moment. For the case illustrated, the twisting moment M

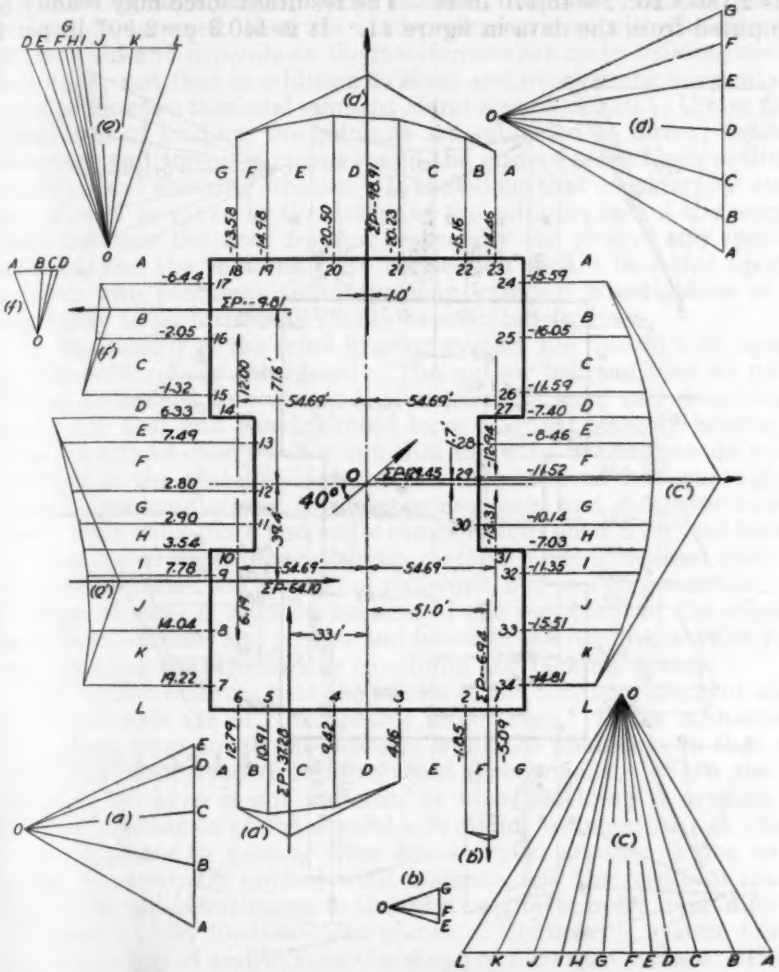

FIGURE 10.—*Graphical representation of pressures exerted on building at section B at setting 40°. Wind in direction of arrow.*

The numbers on the lines through the pressure stations are the values of the force acting on the panel divided by the velocity pressure. The resultants on the several faces are determined graphically in the auxiliary diagrams, *a*, *a'*, *b*, *b'*, etc.

may be obtained by taking moments about O, the trace of the vertical axis of the building, clockwise moments being positive.

Level A (fig. 9) $M/q = -93.49\times22.1-4.10\times75.6+86.82\times1.00$
$-119.64\times2.1+8.36\times47.0+26.68\times30.8$
$-5.79\times51.14+10.44\times51.14+9.06\times51.14$
-8.56×51.14
$= -1{,}062$ ft.^{3}

Similarly at level B, $M/q = -1{,}221$ ft.^{3} and at level C, $M/q = -2{,}180$ ft.^{3}

If the wind velocity is known, the actual moment per ft. of height can be found by multiplying the above figures by the velocity pressure. For example, the velocity pressure for a wind velocity of 90 mph is 20.72 lb per sq ft and hence the moment per ft height at level C is $2{,}180 \times 20.72 = 45{,}170$ lb ft. The resultant force may readily be computed from the data in figure 11. It is 140.3 $q = 2{,}907$ lb per ft

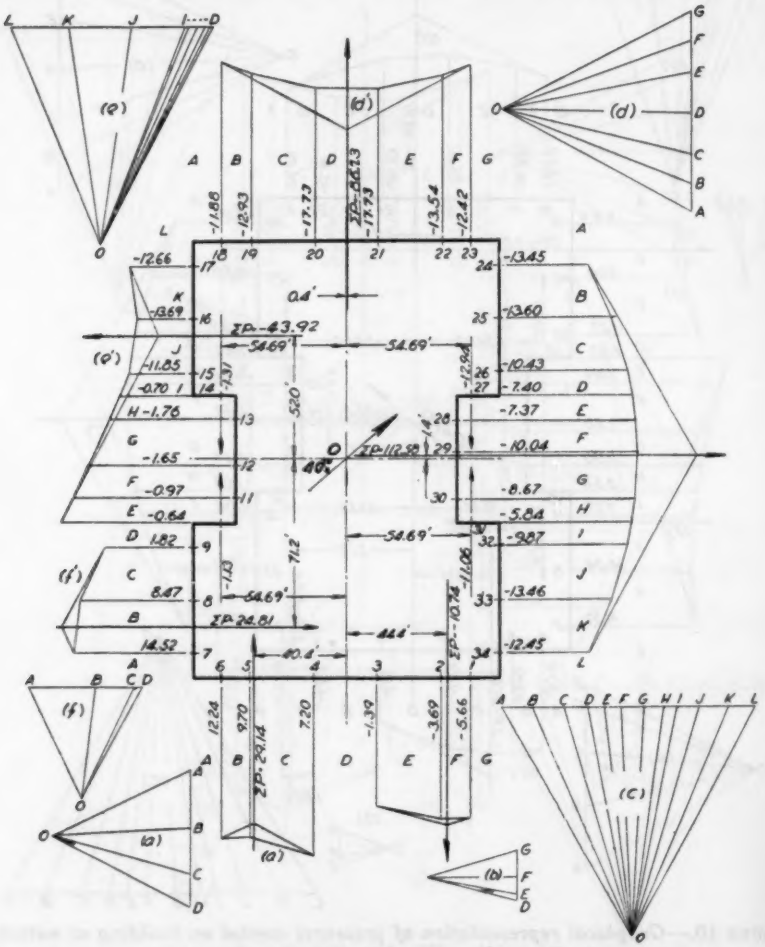

FIGURE 11.—*Graphical representation of pressures exerted on building at section C at setting 40°. Wind in direction of arrow.*

The numbers on the lines through the pressure stations are the values of the force acting on the panel divided by the velocity pressure. The resultants on the several faces are determined graphically in the auxiliary diagrams, *a*, *a'*, *b*, *b'*, etc.

of height. The displacement of the resultant force from the axis of the building is therefore $45{,}170/2{,}907 = 15.5$ ft.

It will be noted that the torque at level C is nearly double that at levels A and B, an effect produced by the presence of the other models.

Analysis of the loading at other angles may be made in a similar manner.

III. ANALYSIS OF THE RESULTS WITH REFERENCE TO THE DESIGN OF TALL BUILDINGS

The measurements show that the wind pressure is distributed over the building in a manner quite different from the uniform loading commonly assumed; that the wind pressure varies with the direction of the wind and depends on the interference set up by existing nearby buildings; and that in addition to shear and overturning moment, the wind produces a torsional moment about a vertical axis. Under these conditions of loading, the columns are subjected to direct, bending, shearing, and torsional stresses, and the girders are subject to direct, bending, and shearing stresses. It is evident that considerable attention should be given to the design of the columns and of the connections between the floor framing, especially the girders and spandrel sections, and the columns. No connection should be relied upon to perform two functions simultaneously without investigation of its capability to perform both functions simultaneously.

In the design of the wind-bracing system the question of rigidity should be carefully considered. The author believes that all panels should be braced to withstand wind pressure from any direction, in particular that end panels should have diagonal or sway bracing, or knee bracing at each column and that the wind bracing should not be confined to the center of high towers. He believes that where girder connections are designed to withstand moment and shear due to wind loads, wide wing-plate and angle combinations should be used instead of the socalled "split flange I-beam method." It is realized that this practice increases the amount of millwork, but as a compensation, the tonnage of steel is reduced because of the reduction of the effective lengths of columns and girders and hence in the required section areas in computing the stresses due to column and bending action.

The author believes that the effects of the torsional moment about a vertical axis are of considerable importance. If the moments at each plane were equal, the problem would be analogous to that of a cantilever beam loaded uniformly but eccentrically. When the distribution of force is not uniform, as when shielding is present, the torsional moments at the several elevations are unequal. A change in the moment in passing from one story to another is due to the action of externally applied wind moment, and the resultant loading of the building is analogous to that of a cantilever beam, nonuniformly and eccentrically loaded. The planes of the flooring system tend to become distorted and to take the shape of a warped surface. Due to the rigidity of the flooring systems commonly used (steel encased in concrete), the stresses in the columns are likely to be the more important.

As an illustration of a failure of a building in a high wind which probably was a failure in torsion, mention may be made of the Meyer-Kiser building in Miami, Fla. A special committee of the American Society of Civil Engineers [7] was appointed to investigate the results of the storm in which this building failed. The top of the building was twisted [8] in a clockwise direction about 1°. Most of the twisting probably occurred between the fifth and thirteenth floors. Little damage

[7] Papers and Discussions A.S.C.E., vol. 54, pt. 2, p. 1757, 1928.
[8] Engineering News Record, vol. 97, pp. 586 and 624, 1926.

was done to floors and ceilings. The committee attributes the twisting in large measure to the fact that one end of the building was stiffer than the other.

The author is indebted to the Bureau of Standards and its director, Dr. Lyman J. Briggs, for the facilities placed at his disposal, to Dr. Hugh L. Dryden, chief, aerodynamical physics section, for helpful criticism and suggestions, and to Mr. W. H. A. Boyd for assistance in making observations and recording data.

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SOIL-CORROSION STUDIES, 1932. RATES OF LOSS OF WEIGHT AND PITTING OF FERROUS AND NON-FERROUS SPECIMENS AND METALLIC PROTECTIVE COATINGS

By K. H. Logan and R. H. Taylor

ABSTRACT

In 1922 the Bureau of Standards began the study of the action of soils on buried pipe. Reports on this investigation have been issued at intervals of approximately 2 years. The first report described the soils and materials under investigation, and the 1930 reports summarized all data then available. This report deals only with data on specimens removed in 1932. Consideration of these data does not materially alter the conclusions reached earlier that the character of the soil controls the rates of corrosion of ferrous materials and that in the same soil all of the commonly used ferrous materials corrode at nearly the same rate.

For the soils investigated, the rate of corrosion in a soil of a given series as identified by the United States Department of Agriculture appears to be characteristic of the series and it seems probable that the rate of corrosion in any location in a soil belonging to a known soil series can be predicted when the corrosiveness at one location in that series has been determined, provided the location of the pipe with respect to the soil horizons of the series is taken into account.

Metallic protective coatings show signs of failure, after 8 years in several of the more corrosive soils. Several non-ferrous metals and alloys are more resistant to soil action than the ferrous materials commonly used.

CONTENTS

	Page
I. Introduction	120
II. Ferrous materials removed in 1932	120
1. Pipe line materials buried in 1922	120
(*a*) Rates of loss of weight	120
(*b*) Rates of penetration by pitting	124
2. Special cast pipe and fittings	125
(*a*) Corrosion of high-silicon cast iron	125
(*b*) Pipe materials buried in 1924	126
III. Estimation of pipe life in terms of experimental data	127
1. Effect of duration of exposure	127
2. Effect of methods of determining rates of corrosion	128
3. Effect of length and diameter of pipe	129
4. Variations in pipe life under apparently similar conditions	130
5. Estimation of rates of corrosion of pipe lines from Bureau data	130
IV. Corrosion at different locations in the same soil series	130
V. Corrosion of non-ferrous metals	134
1. Cast brass and attached nipples	134
2. Copper and copper alloy pipes and rods	135
3. Lead cable sheath	136
4. Parkway cable	137
5. Miscellaneous metals and alloys	138

Page
VI. Corrosion of metallic protective coatings 139
1. Galvanized pipe and sheet 139
2. Relation of weight of zinc to corrosion 142
3. Lead coated pipe 142
4. Calorized pipe 143
5. Sheradized and lead-coated bolts 143
VII. Conclusion 144
VIII. Acknowledgments 144
Appendix 1. Errata in earlier reports 145

I. INTRODUCTION

In 1922 the Bureau of Standards buried 6 sets of specimens of the more commonly used pipe materials in 47 soils for the purpose of studying the effects of soils on buried pipe systems. Later, the original specimens were supplemented by others buried for special purposes. The original plans for these tests called for the removal of sets of specimens at 2-year intervals, but data secured from some of of the test locations indicated that, on account of the low corrosivity of the soils, a less frequent examination of specimens in some locations would be sufficient. In 1932, therefore, specimens were removed only from the more corrosive soils and from such other locations as special conditions called for. The data therefore are not indicative of the average corrosiveness of all soils. If the present plans for the corrosion work are carried out, the last of the original specimens will be removed from the corrosive soils in 1934 and a complete report on the original undertaking will be prepared as soon thereafter as circumstances permit.

The form of the present paper and the method of treating the data are similar to those adopted in previous reports. Since only the 1932 data are here tabulated, the reader must refer to the earlier reports for other information regarding the investigation. In Technologic Paper no. 368 [1] the nature of the investigation, the soils, and materials are described, and in Research Papers nos. 329 [2] and 359 [3] the data obtained up to the end of 1930 are summarized.

A study of these papers is quite essential to a correct interpretation of the data since the results of any experiment depend largely on the conditions under which it is conducted. Some of the relations of the data presented in this and earlier reports to the corrosion of pipe lines are discussed briefly in section III of this report.

II. FERROUS MATERIALS REMOVED IN 1932

1. PIPE LINE MATERIALS BURIED IN 1922

(a) RATES OF LOSS OF WEIGHT

Specimens of the commonly used pipe materials which had been exposed to the more corrosive soils for 10 years were removed from 21 locations. To the data on these specimens have been added the values for specimens buried about 2 years later in another corrosive soil. Table 1 gives the significance of the identification letters for the various materials. The table also contains information on other

[1] Logan, K. H., Ewing, S. P., and Yeomans, C. D., Bureau of Standards soil-corrosion studies: I. Soils, materials, and results of early observations, B.S.Tech. Papers, vol. 22 (T368, 50¢), p. 447, 1928.

[2] Logan, K. H., and Grodsky, V. A., Soil-corrosion studies, 1930: Rates of corrosion and pitting of bare ferrous specimens, B.S.Jour. Research, vol. 7 (RP329, 10¢), p. 1, July 1931.

[3] Logan, K. H., Soil-corrosion studies: Non-ferrous metals and alloys, metallic coatings and specially prepared ferrous pipes removed in 1930, B.S.Jour. Research, vol. 7 (RP359, 10¢), p. 585, September 1931.

materials to be discussed later. In most cases two specimens of each material were removed at each location. Since the specimens differ in diameter and in the duration of exposure it has been necessary, in order to compare different materials and different soils, to reduce the data to rates of loss of weight and penetration by pitting.

TABLE 1.—*Identification of materials*

Identification letters	Material
1¼-INCH PIPE SPECIMENS	
	Tables 2 and 3:
a	Pure open-hearth iron, lap-welded.
b, d	Hand-puddled wrought iron, butt-welded.
e	Bessemer steel, butt-welded.
y	Scale-free Bessemer steel, butt-welded.
3-INCH PIPE SPECIMENS, LAP-WELDED	
	Tables 2, 3, 6, 7:
A [1]	Pure open-hearth iron.
B, D	Hand-puddled wrought iron.
K	Open-hearth steel.
M	Bessemer steel.
N [1]	Bessemer steel, scale-free, butt-welded.
Y	Open-hearth steel, 0.2 percent copper.
6-INCH CAST-IRON PIPE SPECIMENS	
	Tables 2, 3, 5, 6, 7:
A [1]	Southern cast iron.
C	deLavaud centrifugal process.
CC	deLavaud centrifugal process, only outside exposed to soil.
I [1]	Monocast centrifugal process.
L	Pit cast in sand molds, northern ore.
MC	Pit cast iron, machined surfaces (4 in.).
MD	deLavaud cast iron, machined surfaces.
P [1]	Pit cast iron, southern ore.
Z	Pit cast in sand molds, southern ore (rough surfaces).
MISCELLANEOUS FERROUS CASTINGS	
	Tables 4 and 5:
E	2-in. cast steel elbow.
S	2-in. malleable iron elbow.
V	2½-in. O.D. high-tensile cast-iron nipple.
No letter	3-in. high-silicon cast iron.
COPPER AND COPPER ALLOY PIPES AND RODS	
A	7/16-in. nickel brass rod.
B	½-in. I.P.S. Muntz metal pipe.
M	¾-in. copper pipe.
Me	½-in. S.A.E. forged brass ell.
N	7/16-in. copper-aluminum rod.
P	¾-in. copper pipe.

[1] Specimens buried in 1928 for special tests.

TABLE 1.—*Identification of materials*—Continued

CHARACTER AND DIMENSIONS OF MISCELLANEOUS SPECIMENS

Identification letters	Material
	Table 12:
A	Pure open-hearth iron, 2 by 6 by 0.125 in.
S	Copper-bearing steel, 2 by 6 by 0.0625 in.
Z1	Zinc sheet, 99.5 percent pure, 2 by 6 by 0.0625 in.
Z2	Zinc plate, 99.5 percent pure, 2.0 by 6.0 by 0.25 in.
Z3	Corrugated zinc sheet, 12 by 12 by 0.027 in.
P	"Standard" zinc sheet, 2 by 6 by 0.0625 in.
L	Bronze 90–10 Cu-Sn, 2 by 6 by 0.25 in.
B	Brass 70–30 Cu-Zn, 2 by 6 by 0.050 in.
H	Copper sheet, 2 by 6 by 0.050 in.
N	Chemical lead (0.05–0.08 percent Cu, about 0.005 percent Ag), 2 by 6 by 0.25 in.
NN	Hearth refined lead (less than 0.001 percent each of Cu and Ag), 2 by 6 by 0.25 in.
C1	Commercial aluminum, 2 by 6 by 0.0625 in.
C2	Aluminum with 1.5 percent Mn, 2 by 6 by 0.0625 in.
C3	Duralumin, 2 by 6 by 0.0625 in.
D	Wrought-iron nuts and bolts, 3 by 0.75 in.
F	Lead-coated nuts and bolts, 3 by 0.75 in.
G	Sherardized nuts and bolts, 3 by 0.75 in.

GALVANIZED MATERIALS AND WEIGHTS OF COATINGS PER SQUARE FOOT

	Tables 13 and 14:
A	2-in. pure open-hearth iron pipe, 17 inches long, 2.82 oz per sq ft.
D	Wrought-iron pipe, 17 in. long:
	3-in., 3.48 oz per sq ft.
	1¼-in., 4.99 oz per sq ft.
Y	3-in. copper-bearing open-hearth steel pipe, 3.47 oz per sq ft.
	16-gage pure open-hearth iron sheet:
A2	1.79 oz per sq ft.
A3	1.98 oz per sq ft.
A4	2.65 oz per sq ft.
	16-gage copper-bearing sheet steel:
Y2	1.57 oz per sq ft.
Y3	2.15 oz per sq ft.
Y4	2.76 oz per sq ft.
Y5	2.92 oz per sq ft.
B	16-gage Bessemer sheet steel, 1.62 oz per sq ft.
CA	18-gage pure open-hearth iron sheet, 1.87 oz per sq ft.
CB	18-gage Bessemer steel sheet, 1.66 oz per sq ft.
CY	18-gage copper-bearing sheet steel, 2.12 oz per sq ft.

To express the rates of loss of weight in table 2, which is comparable with tables 11, 13, 15, and 17 of Research Paper 329, for the rolled and deLavaud materials, the losses of two specimens of the same size from the same location have been averaged. Only one specimen of northern and southern cast iron was removed from each soil. In some locations "C" specimens were not buried until 1924. The data for these specimens are given in table 5. The average for all the specimens from the same soil is given in the right-hand column. This average is the arithmetical average of all the data on loss of weight given in the same line, and does not take account of the differences in areas of specimens. Although it might be considered more logical to weight the data in accordance with the areas exposed this would give undue weight to the data for certain materials which are represented only by large-size specimens. For example, the total area of the deLavaud specimens in some soils is four times that of the pure open-hearth iron specimens and twice that of the other cast-iron specimens.

Although specimens were not removed in 1932 from the least corrosive soils under investigation, it will be observed from the table that the lowest recorded rate of loss of weight is less than one tenth

of the highest rate. It will be noticed also that except for the 6-inch cast-iron specimens, the rates of loss of weight of the different materials in any one soil are usually of the same order of magnitude. This is best illustrated by the averages at the bottom of the page. The spread of the data which can be attributed to errors and lack of control of conditions is roughly indicated by the differences in rates of loss of 1½- and 3-inch specimens of the same material such as specimens b and B, which were from the same rolling mill. Specimens e and M are both Bessemer steel and should behave similarly. It will be found that, on the average, the differences in loss of weight of specimens of the same material are of the same order as the differences between materials, so far as the rolled materials are concerned. The cast specimens seem to be significantly different from the rolled specimens in a number of soils. This difference between types of materials is more marked with respect to penetration, as will be seen in the section on rates of pitting.

TABLE 2.—*Average rates of loss of weight of 10-year-old specimens of ferrous pipe*

[In ounces per square foot per year]

Soil no.	Soil	Duration of test (years)	1½-inch wrought specimens [1]				3-inch wrought specimens [1]				6-inch cast-iron specimens			Average of all specimens
			a	b	e	y	B	K	M	Y	C[1]	L[2]	Z[2]	
1	Allis silt loam	9.60	0.840	0.976	1.014	0.917	0.976	1.053	0.932	0.945	1.058	1.005	1.126	0.986
3	Cecil clay loam	10.14	.419	.456	.426	.405	.313	.356	.375	.392	(3)	.641	.419	[4].420
8	Fargo clay loam	9.86	.521	.522	.464	.462	.525	.535	.571	.574	.852	1.064	.969	.642
11	Hagerstown loam	10.02	.136	.168	.202	.196	.167	.181	.165	.146	.123	.111	.181	.161
14	Hempstead silt loam	9.88	.383	.649	.457	.536	.502	.404	.463	.367	.335	.577	.601	.479
16	Kalmia fine sandy loam	10.02	.670	.663	.678	.617	.574	.624	.686	.619	(3)	.849	.824	[4].680
18	Knox silt loam	9.79	.285	.360	.327	.339	.303	.351	.318	.299	.359	.493	.475	.355
19	Lindley silt loam	9.71	.314	.331	.333	.298	.318	.297	.319	.305	.266	.306	.514	.327
20	Mahoning silt loam	9.60	.409	.505	.476	.427	.536	.477	.496	.436	.549	.690	.493	.499
22	Memphis silt loam	9.65	.699	.720	.781	.661	.744	.710	.780	.675	.698	.825	.812	.737
23	Merced silt loam	10.18	1.920	2.125	1.897	1.860	1.936	1.940	2.130	2.136	2.912	2.778	6.116	2.523
28	Montezuma clay adobe	7.73	1.507	1.650	1.873	1.948	1.983	2.121	1.707	2.364	(3)	2.809	------	[4]1.996
29	Muck	10.05	1.604	1.336	1.377	1.390	1.485	1.525	1.472	1.549	(3)	1.513	1.727	[4]1.498
32	Ontario loam	9.57	.218	.338	.321	.258	.318	.248	.295	.274	.345	.359	.491	.315
33	Peat	9.66	1.151	1.288	1.186	1.015	1.046	1.029	1.182	1.087	1.342	1.478	1.253	1.187
34	Penn silt loam	9.89	.420	.484	.467	.416	.458	.397	.433	.449	.555	.606	.642	.484
37	St. Johns fine sand	10.06	.900	.857	.800	.767	.820	.862	.848	.954	(3)	.917	.827	[4].855
39	Sassafras silt loam	9.89	.462	.524	.497	.455	.534	.504	.476	.485	.578	.689	.735	.540
40	Sharkey clay	10.04	.689	.722	.727	.598	.811	.719	.923	.748	(3)	1.031	.903	[4].787
42	Susquehanna clay	10.07	1.145	1.058	1.202	1.245	.879	1.105	.925	.913	(3)	1.119	2.169	[4]1.176
43	Tidal marsh	9.91	1.166	1.153	1.063	1.717	1.048	1.134	.989	1.210	1.305	1.152	.950	1.172
45	Unidentified alkali soil	9.85	1.395	1.210	1.210	1.226	1.268	1.326	1.250	1.374	1.536	1.770	------	[4]1.357
46	Unidentified sandy loam	10.15	.397	.461	.477	.404	.429	.353	.421	.387	.440	.392	.797	.507
	Average	------	.767	.807	.794	.789	.781	.794	.789	.813	------	1.008	[4]1.096	------

[1] Average of 2 specimens in each soil.
[2] 1 specimen only in each soil.
[3] Specimens buried late—see table 5.
[4] These averages do not represent all materials or locations.

From the standpoint of service, the rate of loss of weight is not of great importance so far as underground corrosion is concerned, since a pipe which is punctured by corrosion may show less loss of weight than one generally corroded but still serviceable.

TABLE 3.—*Weighted average rates of maximum pitting of 10-year-old ferrous pipe specimens*

(In mils per year)

Soil no.	Soil	Duration of test (years)	1½-in. wrought specimens [1]				3-in. wrought specimens [2]				6-in. cast-iron specimens			Average of all specimens
			a	b	e	y	B	K	M	Y	C [3]	L [4]	Z [4]	
1	Allis silt loam	9.60	6.7	7.6	8.9	9.5	9.4	8.8	8.9	8.2	9.5	19.1	20.8	10.67
3	Cecil clay loam	10.14	11.7	6.9	7.1	7.4	7.2	6.0	7.8	7.7	(5)	15.9	12.8	9.05
8	Fargo clay loam	9.86	7.6	6.6	6.2	5.8	6.1	8.7	6.9	7.5	11.9	19.0	13.7	9.09
11	Hagerstown loam	10.02	7.5	6.0	7.5	7.0	8.3	6.4	6.5	6.7	3.5	3.3	7.1	6.35
14	Hempstead silt loam	9.88	12.1	10.7	13.2	13.2	9.7	9.1	11.2	13.5	5.5	5.5	5.7	9.97
16	Kalmia fine sandy loam	10.02	6.9	6.1	6.4	5.5	6.7	6.4	6.4	6.6	(5)	15.3	13.5	7.98
18	Knox silt loam	9.79	4.7	4.7	5.2	5.9	4.9	6.4	5.0	4.5	6.2	11.2	12.9	6.50
19	Lindley silt loam	9.71	6.4	5.3	6.3	5.6	5.6	6.7	6.6	7.1	5.9	10.7	15.0	7.38
20	Mahoning silt loam	9.60	3.3	5.4	4.0	3.3	4.2	3.7	4.1	3.5	7.7	10.8	7.3	5.21
22	Memphis silt loam	9.65	5.2	6.4	5.6	5.9	6.8	6.5	6.3	6.5	8.6	12.1	15.7	7.78
23	Merced silt loam	10.18	14.6	17.8	14.5	15.3	13.1	14.7	13.1	15.2	16.9	20.7	31.5	17.04
28	Montezuma clay adobe	7.73	17.7	16.0	15.5	12.4	16.4	20.0	14.5	18.9	(5)	15.7	-----	16.34
29	Muck	10.05	16.2	9.7	7.3	9.2	7.9	11.0	8.8	15.3	(5)	13.0	14.7	11.31
32	Ontario loam	9.57	4.5	5.7	4.8	4.6	5.1	5.0	5.4	8.6	6.4	5.4	6.8	5.66
33	Peat	9.66	11.9	8.6	9.5	7.7	10.7	10.1	10.6	11.0	11.1	15.0	17.7	11.26
34	Penn silt loam	9.89	8.2	4.8	8.4	9.6	6.6	6.9	7.3	10.2	8.2	8.3	8.6	7.92
37	St. Johns fine sand	10.06	6.9	7.1	8.9	7.3	7.3	6.8	8.0	10.8	(5)	5.8	9.1	7.80
39	Sassafras silt loam	9.89	6.9	4.3	4.3	5.2	5.0	6.6	5.3	8.1	7.5	8.0	6.9	6.19
40	Sharkey clay	10.04	7.5	6.2	8.7	6.2	5.9	6.8	5.9	7.5	(5)	7.0	8.8	7.03
42	Susquehanna clay	10.07	8.3	8.4	10.3	9.2	9.3	12.1	9.8	9.9	(5)	13.3	18.7	10.93
43	Tidal marsh	9.91	11.4	7.7	7.1	7.4	13.0	9.5	10.3	13.7	15.7	7.2	9.1	10.19
45	Unidentified alkali soil	9.85	14.6	11.5	14.0	11.9	11.3	13.7	12.8	15.2	13.5	19.9	-----	13.34
46	Unidentified sandy loam	10.15	7.3	9.3	6.7	8.2	7.6	6.0	7.8	7.4	4.2	3.6	7.9	6.91
	Average	-----	9.04	7.95	8.28	7.97	8.18	8.60	8.23	9.72	-----	11.56	12.59	-----

[1] Average of the deepest pit on each of 2 specimens.
[2] Average of the 2 deepest pits on each of 2 specimens.
[3] Average of the 4 deepest pits on 1 specimen.
[4] Specimens buried late. See table 5.

(b) RATES OF PENETRATION BY PITTING

Table 3 shows the rates of penetration of the 10-year-old specimens. It is comparable with tables 12, 14, 16, and 18 of Research Paper 329. For 1½-inch specimens the values for rates of pitting are derived from the average of the single deepest pit on each of 2 specimens. For the 3-inch specimens the average of the 2 deepest pits on each of 2 specimens was taken. For the 6-inch specimens, 4 pits were averaged on each specimen, but there were removed from each soil only 1 "L" and 1 "Z" specimen. An examination of table 3 will make it clear that no one rolled material is outstanding in its resistance to all soils. Previous reports show that for any one period certain materials have lower rates of penetration in certain soils, but it is difficult to determine whether this apparent superiority is real. For example, in table 3, in soil no. 1, specimen "a" shows a rate of pitting lower than any other material in the same soil. This material showed next to the lowest rate of pitting in the same soil for the 8-year period. For the two preceding periods, however, its rates of pitting in the same soil were higher than the average rate found for the rolled materials. It is doubtful, therefore, that the performance of this material is significantly different from that of other materials in the soil. It seems more probable that the character of the test makes it impossible to detect small differences in the behavior of different materials. In certain cases, however, the differences are of sufficient magnitude

to be significant. It is probable that any large differences in the behavior of different materials would be clearly evident from the data. It should be remembered, however, that there are no great differences in the composition of the rolled materials under consideration. The economic importance of such differences in materials as are now apparent or may appear when additional data have been obtained depends on the conditions under which the material is to be used. For example, if the cost of the pipe in an installation is but a small fraction of the cost of the complete structure, as when a gas or water service is laid under a city pavement, a small increase in the life of the material may justify a very considerable expenditure, especially if the rate of corrosion is high.

There is little doubt that underground corrosion is an electrochemical process and that strains, impurities, and segregation cause potential differences which influence the rate of corrosion, but it must be remembered that when commercial materials are used as received from the rolling mill (except for the removal of grease, shop coating, and dirt) there is a relatively large potential difference between the oxidized surface and the unoxidized metal for any material and that other potential differences are inevitably set up on account of unequalities in the supply of oxygen as the soil shrinks and swells with changes in moisture content. The data indicate that soil conditions control the rate of corrosion of buried ferrous metals. Soil conductivity, soil acidity, moisture, and oxygen supply have been suggested as factors influencing corrosion. Whether these are the elementary factors or the results of more fundamental causes is not definitely known. An attempt to correlate the corrosion data with the physical and chemical characteristics of the soils is in progress.

2. SPECIAL CAST PIPE AND FITTINGS

(a) CORROSION OF HIGH-SILICON CAST IRON

In addition to specimens of the more commonly used pipe materials, specimens of high-silicon cast iron were also buried. This material is used primarily in connection with the manufacture and use of corrosive chemicals and would not be chosen for the transportation of oil, water, or gas under normal conditions because of its cost and the difficulties in making connections with it. As will be seen from table 4, the rates of loss of weight are relatively very low in all soils. In 1932 as well as on previous occasions, there were a very few specimens showing 1 or 2 deep pits. These pits have been attributed to flaws or the corrosion of segregated areas rather than to the action of soils on the normal metal. At variance with this explanation, however, is the fact that the worst pitting occurred in the same soil both in 1930 and in 1932, and on each occasion both specimens were affected. In another soil a deep pit occurred on 1 specimen in 1930 and on 1 in 1932.

TABLE 4.—*Average rates of loss of weight of high-silicon cast iron specimens*

Soil no.[1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year [2]	Soil no.[1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year [2]
1	9.60	0.0070	29	10.05	[4] 0.0430
3	8.13	[3] .0011	32	9.57	[3] .0148
8	9.86	[4] .0054	33	9.66	.0621
11	10.02	.0026	34	9.89	.0370
14	9.88	.0024	37	8.06	.0386
16	8.06	.0021	39	9.89	.0026
18	9.79	.0023	40	10.04	[3] .0163
19	9.71	.0030	42	10.07	.0034
20	9.60	[3] .0346	43	9.91	.2519
22	9.65	.0070	45	9.85	.0225
23	10.18	.0057	46	10.15	.0041
28	([5])	([5])			

[1] For names of soils see table 2.
[2] Average of 2 specimens except as noted.
[3] 1 specimen only. Companion specimen chipped or broken.
[4] 1 specimen only.
[5] Softened at one or more points.
[6] Both specimens chipped and corroded.

(b) PIPE MATERIALS BURIED IN 1924

Two years after the first test was started, it was decided to bury a group of cast materials sponsored by the American Foundrymen's Association. Since attention had been called to the fact that the inside surface of deLavaud cast iron differed somewhat from the outside surface it was decided to bury additional samples of this material with the outside surface only exposed to soil. To determine the effect of the surface layers on the two kinds of cast iron, specimens of deLavaud and pit cast iron with machined surfaces were provided for six soils. The results of the 1932 examination of these specimens are given in table 5. The data on the pit cast specimens P may be used as a guide for correlating this table with the tables previously given.

The data are inadequate for determining the relative merits of the materials, but the following indications may be noted. Removing the original surface from the deLavaud specimens apparently did not affect the rate of pitting. On the average, the machined pit cast-iron specimens MC behaved similarly to the unmachined pit cast specimens P, but the pits on the machined specimens were deeper in 4 out of 5 soils. The high-tensile cast iron (V) appears to behave similarly to ordinary cast iron (P).

The cast steel specimens and the malleable iron specimens were in the form of elbows and on account of the double curvature of their surfaces, it was impossible to determine pit depth on these materials with the apparatus at hand. The rates of loss of weight of these materials are about the same as those of the pit cast-iron specimens and visual inspection shows no marked differences in rates of pitting when the elbows are compared with other materials in the same soil. While there are apparent differences in the rates of corrosion of the cast-steel and malleable-iron specimens, in some soils one appears better, and in other soils the other appears better. It is doubtful whether the differences shown in the table are significant.

TABLE 5.—*Corrosion of special cast iron pipes and fittings*

(A) RATES OF LOSS OF WEIGHT OF SPECIAL CAST SPECIMENS

[In ounces per square foot per year]

Soil no.	Soil	Duration of test (years)	Specimens [1]							
			P	CC	I [2]	MD	MC	V	E	S
3	Cecil clay loam	8.13	------	0.366	------	------	------	------	------	------
13	Hanford very fine sandy loam	8.25	0.949	1.399	------	1.139	1.780	1.278	1.260	0.889
16	Kalmia fine sandy loam	8.06	------	1.431	------	------	------	------	------	------
28	Montezuma clay adobe	7.73	3.020	1.628	------	------	------	------	2.530	2.404
29	Muck	8.10	1.510	[3] 2.09	------	1.31	1.34	1.31	1.200	1.140
37	St. Johns fine sand	8.06	------	1.134	------	------	------	------	------	------
40	Sharkey clay	8.09	------	9.54	------	------	------	------	------	------
42	Susquehanna clay	8.08	.419	.456	------	.503	.619	.596	.557	.725
43	Tidal marsh	8.63	1.100	2.004	------	1.991	1.272	1.464	.679	.927
45	Unidentified alkali soil	8.70	2.075	2.510	------	2.374	1.945	2.020	1.847	1.575

(B) WEIGHTED MAXIMUM RATE OF PITTING

[In mils per year]

3	Cecil clay loam	8.13	------	7.4	------	------	------	------	------	------
13	Hanford very fine sandy loam	8.25	20.2	15.7	16.8	12.0	[4] 30.3	23.1	[5] Sa	Sa
16	Kalmia fine sandy loam	8.06	------	13.1	------	------	------	------	------	------
28	Montezuma clay adobe	7.73	41.6	[3] 16.6	[3] 33.8	------	------	------	Pa	Pa
29	Muck	8.10	11.7	[3] 9.7	6.4	9.2	13.7	12.6	Pa	Pa
37	St. Johns fine sand	8.06	------	5.1	------	------	------	------	------	------
40	Sharkey clay	8.09	------	8.52	------	------	------	------	------	------
42	Susquehanna clay	8.08	13.6	9.2	11.0	9.5	17.7	13.3	Sa	Pb
43	Tidal marsh	8.63	25.3	15.2	22.8	15.2	14.2	15.7	Sb	Pb
45	Unidentified alkali soil	8.70	15.6	12.2	7.3	[4] 22.6	[4] 25.4	20.1	Pa	Sa

[1] See table 1 for names of materials.
[2] Specimens partly coated with cement.
[3] One specimen only.
[4] Punctured.
[5] C, no pitting; S, slight pitting; P, general pitting; a, specimens about the same as others in the same soil; b, specimens better than others in the same soil; w, specimens worse than others in the same soil.

III. ESTIMATION OF PIPE LIFE IN TERMS OF EXPERIMENTAL DATA

Since the principal use to which the data in this and similar reports will be put is the estimation of the life of pipe underground, it is important to call attention to the fact that the data here presented are, strictly speaking, directly applicable only to specimens of similar sizes exposed for equal periods to similar soil conditions. In order to make practical applications of the data it is necessary to take into account the differences in the conditions of exposure of the specimens reported on and the pipe line under consideration.

1. EFFECT OF DURATION OF EXPOSURE

It has been shown in previous reports that the rate of corrosion decreases with the time of exposure in most soils. This is shown in figures 1 to 4 in which the average total depths of the deepest pits on the rolled specimens have been plotted for each period for the soils from which specimens were removed in 1932. The pit depths have been weighted as explained in the discussion of table 3. The curves serve three purposes. (1) They show the spread of the data and hence indicate their reproducibility. The significance of this will be dis-

cussed a little later. (2) They show that the corrosiveness of soils differs widely. (3) They show that for most soils the curves bend downward, which indicates that usually the rate of penetration decreases as the period of exposure increases. From this it follows that the life of a pipeline cannot be estimated from data for a single period of exposure such as those in table 3. It is necessary to know also

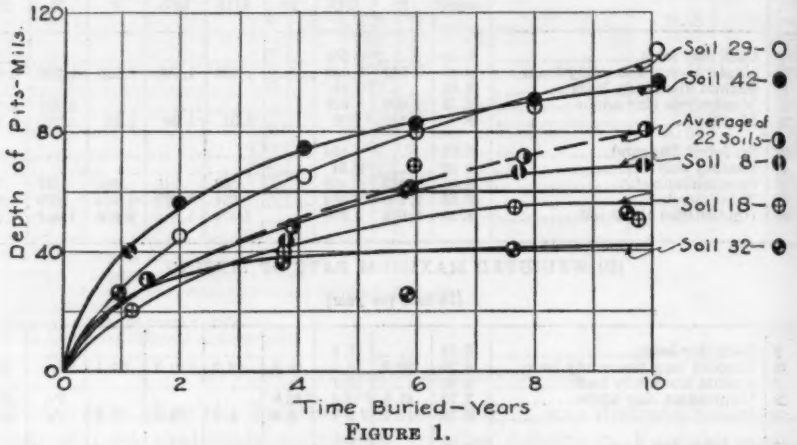

FIGURE 1.

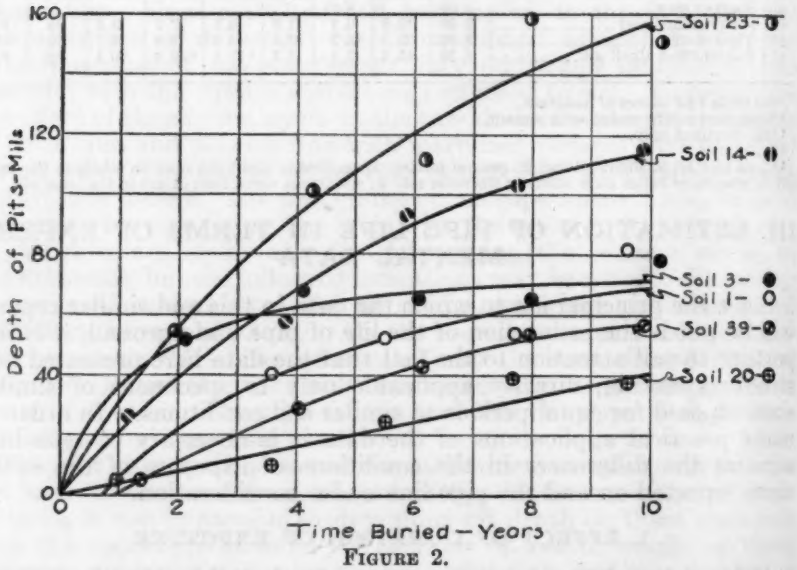

FIGURE 2.

the effect of time on the rate of corrosion. The change in rate of penetration is not the same for all soils.

2. EFFECT OF THE METHODS OF DETERMINING RATES OF CORROSION

The value of the rate of corrosion will, of course, depend upon the way in which it is determined. The data given in table 3 as weighted maximum rates of penetration are actually the averages of the depths of from 2 to 8 pits on 2 specimens 6 inches long and from 1½ to 6 inches

in diameter. The data used for plotting the curves in figures 1 to 4 are the averages of the depths of 24 pits on a total area of about 5 square feet of pipe surface. Obviously, if the single deepest pit on say a 30-foot length of 10-inch pipe had been taken as the basis for expressing the rate of penetration, a considerably larger value would have been found under the same soil condition.

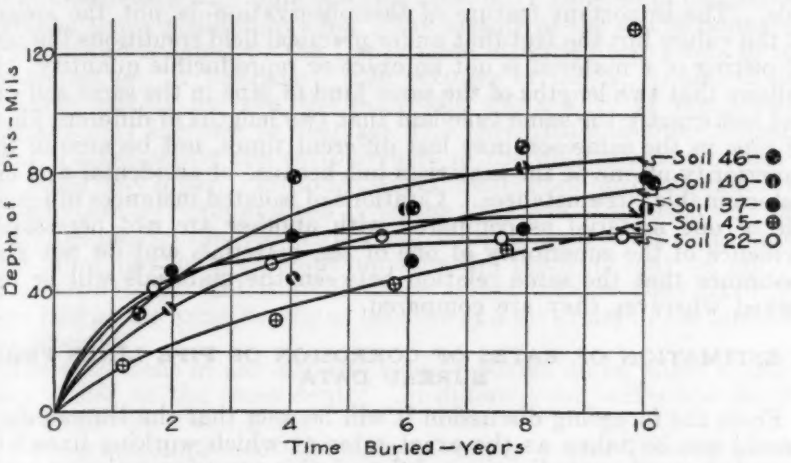

FIGURE 3.

3. EFFECT OF LENGTH AND DIAMETER OF PIPE

In addition to the fact that the maximum depth of pit will probably increase with the area exposed, there are other reasons for expecting that the maximum depth of pit on a pipe line will be somewhat greater

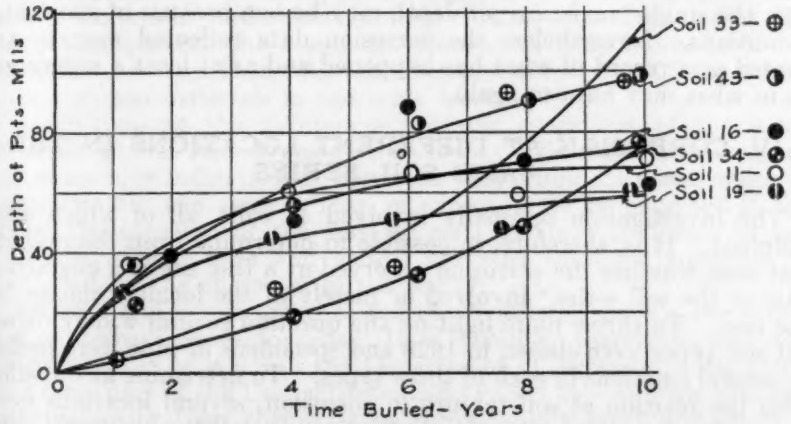

FIGURE 4.

than is indicated by the specimens in this report for the same soil conditions. The top and bottom of a pipe of large diameter will probably be exposed to different conditions with respect to both soil and moisture, and these differences will result in galvanic potentials and increased corrosion. Galvanic potentials will likewise be created because the pipe line will pass through different soils. The pipe may also be connected to metals which are cathodic to it.

4. VARIATIONS IN PIPE LIFE UNDER APPARENTLY SIMILAR CONDITIONS

A comparison of the data for different specimens of the same material, such as those for wrought-iron or Bessemer steel, in the same soil and with the same period of exposure indicates quite clearly that there are rather wide limits within which the results are not reproducible. The important feature of this observation is not the spread of the values but the fact that under practical field conditions the rate of pitting of a material is not an exact or reproducible quantity. It follows that two lengths of the same kind of pipe in the same soil will not last exactly the same time and that two lengths of different kinds of pipe in the same soil may last different times, not because of the superiority of one of the materials but because of accidental and undeterminable circumstances. Citations of isolated instances of longer life of one material as compared with another are not necessarily evidence of the superiority of one of the materials and do not give assurance that the same relation between the materials will be observed wherever they are compared.

5. ESTIMATION OF RATES OF CORROSION OF PIPE LINES FROM BUREAU DATA

From the foregoing discussion it will be seen that the Bureau data should not be taken as the exact rates at which working lines will corrode but only as indications of the relative corrosion-resisting properties of the materials tested and the relative corrosiveness of the soils investigated. It is not possible to reduce the experimental data to rates of corrosion of operating lines by the application of a reduction factor because the conditions under which each pipe line is laid are different. On the average, the maximum rate of corrosion of a pipe line will be greater than that given in this report, but in a given location the single maximum pit depth may be less because of accidental conditions. Nevertheless the corrosion data collected may be accepted as a record of what has happened and as at least a suggestion as to what may happen again.

IV. CORROSION AT DIFFERENT LOCATIONS IN THE SAME SOIL SERIES

The investigation originally involved 47 soils, all of which were different. It is, therefore, impossible to determine from the original test data whether the corrosion observed at a test site is a characteristic of the soil series [4] involved or merely of the locality chosen for the test. To throw more light on the question several widely different soil types were chosen in 1928 and specimens of pipe were buried at several locations in each of these types. To determine at the same time the relation of soil texture to corrosion, several locations were chosen in the same soil series but where the textures differed. In addition, locations were chosen in which the character of the salts was the same but the amount of the salts differed. Unfortunately, in order to secure different amounts of salts in any one soil series, it was necessary to choose locations differing in texture or drainage and the effect of differences in the amounts of salts may be obscured by the other differences mentioned.

[4] Soils alike in all particulars except texture are said to belong to the same series. If they are alike in texture also they belong to the same type.

In attempting to determine whether the rate of corrosion throughout the areas mapped as a single soil type or series is the same or in trying to predict the rate of corrosion at one point in a given soil series from the known rate of corrosion at some other point in the same series, several things must be kept in mind: The rate of corrosion usually decreases with time and this must be considered in comparing corroded pipes of different ages. The texture of the soil as indicated in the names assigned by the Department of Agriculture refers to the uppermost or "A" horizon. The textures of the A, B, and C soil horizons usually are not the same and the acidity of the several horizons may increase or decrease with their distance from the surface. Consequently the corrosiveness of the different horizons of a soil series may differ. Although within limits each horizon is uniform in its nature throughout a soil type, the thickness of the horizons and their distances from the surface vary because of local conditions. Two pipes may lie in different horizons and therefore may be subject to somewhat different soil conditions either because they have not been laid at the same depths or because at a given depth the horizons are different.

The specimens in any one soil series reported on in tables 6 and 7 were placed at the same depth. In different soil series the depths varied between 2 and 5 feet.

Since consideration of the data of tables 6 and 7 leads to the same general conclusions, the discussion of them will be confined mostly to table 7. This table is in agreement with table 3 in its indication that in a given soil the rates of penetration of the different rolled materials are similar.

To determine whether or not the data show significant differences between the individual soils of a series, the best available criterion is the consistency of the apparent differences with respect to the several materials under observation. Using the Cecil series for illustration because the maximum amount of data is available for this series, one sees that with the exception of soil no. 105 the differences between materials in the same location are of the same order of magnitude as the differences between specimens of the same materials in different types of the series. The data for the other soil series also indicate that corrosion throughout any one series is approximately the same. This, of course, is to be expected if the actual classification of the soils at each location conforms to the definition of soil type and series, provided that the corrosion is controlled by the character of the soil.

Tables 6 and 7 indicate that soil characteristics govern the corrosion of ferrous pipes in soils. It is possible, therefore, that the classification of soils which the Department of Agriculture has made for a large part of the United States can be used to obtain an approximate value for their corrosiveness throughout a given soil series if the rate of corrosion at one location in the series has been determined. The Bureau of Standards is obtaining such data for approximately 50 soil series. The Department of Agriculture has defined about 1,500 different series. Since the rate of corrosion is affected by local soil conditions and by factors independent of the soil, only approximate values for rates of corrosion can be hoped for and it is probable that, since this is all that is expected, many soil series can be grouped together as being similar with respect to corrosivity

provided that the relationship between corrosion and the chemical and physical properties of soils can be determined. An investigation is now under way to see whether or not this can be done.

TABLE 6.—*Relation of soil series to rates of loss of weight of ferrous specimens*

Soil no.	Soil	Location	Duration of test (years)	Rates of loss in ounces per square foot per year					
				Materials [1]					
				A	B	N	P	I	Average
101	Billings silt loam [2]	Grand Junction, Colo.	4.07	1.720	2.154	1.776	2.028	1.934	1.922
102	do.[3]	do	4.07	2.304	2.508	2.278	2.872	2.275	2.447
103	do.[4]	do	4.07	2.755	2.699	2.480	7.057	6.907	4.380
	Average			2.260	2.454	2.178	3.986	3.705	2.910
104	Cecil clay	Charlotte, N.C.	4.10	1.168	1.044	1.031	.982	.894	1.024
3	Cecil clay loam	Atlanta, Ga.	4.09	.705	.885	.875	1.030	.....	[5].874
105	do	Macon, Ga.	4.03	.884	.931	1.030	1.101	1.064	1.002
106	do	Salisbury, N.C.	4.10	.819	.982	.879	1.301	1.218	1.040
107	Cecil fine sandy loam	Raleigh, N.C.	4.10	.709	.790	.755	.754	.604	.722
108	Cecil gravelly loam	Atlanta, Ga.	4.02	.764	.886	.851	1.257	1.290	1.010
	Average			.842	.920	.904	1.071	[5]1.014	[5].945
109	Fresno fine sandy loam [2]	Kerman, Calif.	4.01	1.979	1.902	1.571	3.319	2.883	2.331
110	do.[3]	do	4.01	1.903	1.766	1.843	2.472	2.459	2.089
111	do.[4]	Kernell, Calif.	3.66	2.383	2.133	2.388	2.487	2.990	2.476
	Average			2.088	1.934	1.934	2.759	2.777	2.299
112	Imperial clay [2]	Niland, Calif.	4.01	3.611	3.375	3.505	4.501	4.695	3.937
113	do.[4]	do	4.01	4.737	3.991	4.605	6.572	7.979	5.577
	Average			4.174	3.683	4.055	5.536	6.337	4.757
114	Lake Charles clay	El Vista, Tex.	2.96	1.637	2.045	1.685	1.495	1.412	1.655
22	Memphis silt loam	Memphis, Tenn.	3.68	.870	.980	.955	1.115	.....	[5].980
115	do	Vicksburg, Miss.	4.11	.594	.699	.657	.793	.662	.681
	Average			.732	.840	.806	.954	.....	[5].830
23	Merced silt loam	Buttonwillow, Calif.	4.27	2.620	2.800	2.805	6.745	.....	3.743
116	Merced clay	Los Banos, Calif.	4.04	3.217	2.909	2.847	4.603	4.501	3.615
117	Merced clay loam adobe	Tranquillity, Calif.	4.04	2.372	2.450	2.331	3.728	3.062	2.789
	Average			2.736	2.720	2.661	5.025	3.782	3.382
118	Niland gravelly sand	Niland, Calif.	4.01	3.040	2.725	3.261	3.992	[5]4.330	[5]3.470
119	Norfolk sandy loam	Macon, Ga.	4.03	.980	1.070	1.131	1.159	1.139	1.096
120	Norfolk sand	Pensacola, Fla.	4.05	.232	.231	.211	.174	.195	.209
121	do	Tampa, Fla.	4.04	.251	.217	.175	.132	.182	.191
31	do	Jacksonville, Fla.	4.07	.500	.510	.510	.450	.....	[5].493
	Average			.491	.507	.507	.479	[5].505	[5].497
122	Panoche clay loam	Mendota, Calif.	4.05	.680	.789	.881	.871	.611	.766
42	Susquehanna clay	Meridian, Miss.	4.07	1.095	1.190	1.255	2.285	.....	[5]1.456
123	do	Shreveport, La.	4.12	1.349	1.565	1.342	1.589	1.595	1.488
124	Susquehanna silt loam	Troup, Tex.	2.74	1.628	1.810	1.912	2.012	1.805	1.833
125	Susquehanna fine sandy loam	Shreveport, La.	4.12	1.191	1.098	1.120	1.449	1.529	1.277
	Average			1.316	1.416	1.407	1.834	[5]1.643	[5]1.514
12	Hanford fine sandy loam	Los Angeles, Calif.	6.17	.520	1.540	.440	.360	.....	.465
13	Hanford very fine sandy loam	Bakersfield, Calif.	5.83	1.110	1.253	1.330	2.163	.....	1.464
26	Miami silt loam	Springfield, Ohio	7.67	.265	.225	.245	.410	.....	.286
25	Miami clay loam	Milwaukee, Wis.	7.62	.290	.310	.300	.345	.....	.311
	Average			.277	.267	.272	.377	.....	.298

[1] See table 1 for identification of materials.
[2] Low alkali.
[3] Moderate alkali.
[4] High alkali.
[5] These averages do not represent all materials.

TABLE 7.—*Relation of soil series to weighted rates of maximum pitting of ferrous specimens*

Soil no.	Soil	Location	Duration of test (years)	Rates of penetration in mils per year					
				Material [1]					
				A	B	N	P	I	Average
101	Billings silt loam [2]	Grand Junction, Colo.	4.07	27.8	21.6	22.8	20.9	23.6	23.3
102	do.[3]	do	4.07	22.8	19.2	16.5	26.1	23.3	21.6
103	do.[4]	do	4.07	21.6	20.9	16.0	38.6	46.7	28.8
	Average			24.1	20.6	18.4	28.5	31.2	24.6
104	Cecil clay	Charlotte, N.C.	4.10	19.8	21.0	22.2	16.2	18.5	19.5
3	Cecil clay loam	Atlanta, Ga.	4.09	18.0	14.9	16.9	15.4	-----	[5] 16.3
105	do	Macon, Ga.	4.03	11.9	11.9	11.2	30.0	31.3	19.3
106	do	Salisbury, N.C.	4.10	14.9	13.9	12.9	27.3	24.4	18.7
107	Cecil fine sandy loam	Raleigh, N.C.	4.10	17.1	17.3	15.4	13.9	15.9	15.9
108	Cecil gravelly loam	Atlanta, Ga.	4.02	19.4	12.2	15.2	32.0	32.1	22.2
	Average			16.9	15.2	15.6	22.5	[5] 24.4	[5] 18.7
109	Fresno fine sandy loam [2]	Kerman, Calif.	4.01	17.7	20.0	15.5	44.6	29.9	25.5
110	do.[3]	do	4.01	20.4	21.2	16.2	44.6	22.2	24.9
111	do.[4]	Kernell, Calif.	3.66	25.7	21.0	21.3	30.9	20.5	23.9
	Average			21.3	20.7	17.7	40.0	24.5	24.8
112	Imperial clay [3]	Niland, Calif.	4.01	45.9	31.2	31.7	54.2	69.8	46.6
113	do.[4]	do	4.01	53.9	37.4	51.6	58.5	52.6	50.8
	Average			49.9	34.3	41.6	51.3	61.2	48.7
114	Lake Charles clay	El Vista, Tex.	2.96	32.4	24.0	17.9	4.2	8.8	17.5
22	Memphis silt loam	Memphis, Tenn.	3.68	12.0	14.6	13.5	23.9	-----	[5] 16.0
115	do	Vicksburg, Miss.	4.11	13.9	11.4	11.4	14.6	15.6	13.4
	Average			13.0	13.0	12.5	19.3	-----	[5] 14.7
23	Merced silt loam	Buttonwillow, Calif.	4.27	22.0	22.3	24.5	55.1	-----	[5] 31.0
116	Merced clay	Los Banos, Calif.	4.04	23.8	23.5	21.8	42.5	38.1	29.9
117	Merced clay loam adobe	Tranquillity, Calif.	4.04	31.2	27.5	24.3	40.0	31.4	30.9
	Average			25.7	24.4	23.5	45.9	34.8	30.6
118	Niland gravelly sand	Niland, Calif.	4.01	36.4	29.9	29.2	51.9	[5] 49.4	[5] 39.4
119	Norfolk sandy loam	Macon, Ga.	4.03	20.1	12.7	16.1	31.9	27.5	21.7
120	Norfolk sand	Pensacola, Fla.	4.05	4.2	2.5	2.5	2.5	2.5	2.8
121	do	Tampa, Fla.	4.04	7.2	2.5	2.5	2.5	2.5	3.4
31	do	Jacksonville, Fla.	4.07	6.0	7.2	6.4	8.1	-----	[5] 6.9
	Average			9.4	6.2	6.9	11.3	[5] 10.8	[5] 8.7
122	Panoche clay loam	Mendota, Calif.	4.05	11.6	12.8	9.1	9.5	11.4	10.9
42	Susquehanna clay	Meridian, Miss.	4.07	16.0	19.2	19.3	32.6	-----	[5] 21.8
123	do	Shreveport, La.	4.12	10.4	9.0	10.2	23.9	11.7	13.0
124	Susquehanna silt loam	Troup, Tex.	2.74	19.3	18.6	19.7	21.5	19.0	19.6
125	Susquehanna fine sandy loam	Shreveport, La.	4.12	12.9	10.2	10.9	19.4	15.8	13.8
	Average			14.7	14.3	15.0	24.4	[5] 15.5	[5] 17.0
12	Hanford fine sandy loam	Los Angeles, Calif.	6.17	9.0	10.4	9.8	6.4	-----	-----
13	Hanford very fine sandy loam	Bakersfield, Calif.	5.83	8.0	9.6	8.4	30.0	-----	-----
	Average			8.5	10.0	9.1	18.2	-----	-----
26	Miami silt loam	Springfield, Ohio	7.67	5.1	5.5	6.2	8.3	-----	-----
25	Miami clay loam	Milwaukee, Wis.	7.62	4.9	6.8	5.9	9.8	-----	-----
	Average			5.0	6.1	6.0	9.0	-----	-----

[1] See table 1 for identification of materials.
[2] Low alkali.
[3] Moderate alkali.
[4] High alkali.
[5] These averages do not represent all materials.

Sometimes the rules for the designation of a soil series do not take account of all factors affecting the soil. This is the case with respect to the amount of soluble salts which a soil may contain and under some circumstances with respect to the amount and distribution of rainfall. This is illustrated in table 6 by the differences in the rate of loss of weight of specimens in the two soils of the Hanford series. The more corrosive soil at Bakersfield, soil no. 13, contains a considerable amount of soluble salts. In view of the difference in the corrosiveness of the two soils in the Hanford series it is evident that in using data from one location to estimate the corrosiveness of a soil of the same series at another location, it is necessary to make sure that there is no difference in soil characteristics and that only one soil horizon is involved.

V. CORROSION OF NON-FERROUS METALS

1. CAST BRASS AND ATTACHED NIPPLES

One of the ways suggested for avoiding the losses arising from corrosion when ferrous materials are used is the substitution of a more corrosion-resistant material. Copper alloys and lead have been employed for this purpose to a limited extent for a long time. The early use of brass was for cocks, valves, and valve parts. In many instances cast brass was connected to other metals and it is possible that the differences of potential arising from the combination may have resulted in accelerated corrosion of one of the materials involved. To study this problem, specimens of four cast-copper alloys were connected to short lengths of brass, galvanized iron, and lead pipe and buried in all of the 47 test sites in 1924. Specimens of these materials were removed from 22 soils in 1932. Since there appeared to be no significant difference in the behavior of the copper alloys, although they varied considerably in composition, the losses of the 12 castings in each soil have been averaged. The results are given in table 8. It will be seen that the rate of loss of weight of the caps is very low in all soils except the tidal marsh (soil 43), where it is of the same order of magnitude as that for ferrous materials in moderately corrosive soils. In two soils the rate of loss of weight of the lead nipples attached to the brass caps was very high and in several other soils it approached the rate for ferrous materials. A large proportion of the lead nipples showed about the same rate of corrosion as that of unattached strips of lead in the same soils, as will be seen by comparing the data with those for the H specimens in table 10. In a few locations the rate of corrosion was considerably greater or less than that of the unattached lead specimens, but it seems probable that the differences were accidental.

The corroded brass nipples, which are of Muntz metal, were inadequately cleaned. It was discovered this year that there existed between the bright surface heretofore assumed to be the unaffected material, and the actual unaffected part of the specimen, a dark-red spongy substance which was rather soft and brittle. This substance was found to exist in almost every specimen, regardless of the corrosiveness of the soil from which the specimen was taken. It ranged in amount from a very thin layer to almost the entire thickness of the specimen according to the corrosiveness of the soil. For this reason losses of weight reported in table 8 on these nipples are in

most cases much too small. Since Muntz metal unconnected with anything else has shown much the same deterioration in some soils it is doubtful that much of the corrosion of the nipples can be attributed to galvanic action between the nipples and the cast caps.

TABLE 8.—*Rates of loss of weight of cast-brass caps and of lead, brass, and galvanized nipples attached to the caps*

Soil number [1]	Duration of test (years)	Loss in ounces per square foot per year			
		Avg. of 12 brass caps	Avg. of 4 lead nipples	Avg. of 4 brass nipples	Avg. of 4 galvanized steel nipples
1	8.62	0.007	[2] 2.770	([3])	[4] 2.200
3	8.13	.010	[5] .495	0.051	.322
8	8.73	.008	[2] .101	.136	.503
11	8.66	.014	[4] .412	.057	.298
13	8.25	.007	.208	[4] .122	[2] .806
14	8.76	.003	.459	.034	.213
16	8.06	.007	[2] .142	.141	.500
18	8.60	.004	[4] .195	.032	.275
19	8.59	.009	[4] .402	.076	.266
20	8.62	.008	.594	.133	[4] .331
23	8.25	[6] .040	[6] .168	([3])	([7])
28	7.73	[6] .008			
29	8.10	.022	2.163	([3])	1.514
32	8.63	.008	[2] .123	[4] .057	[4] .122
33	8.63	.038	[4] .223	.393	[4] .547
37	8.06	.033	[4] .626	.202	1.065
39	8.51	.043	[4] .462	.277	.506
40	8.09	[9] .001	[2] .512	.131	([10])
42	8.08	.009	[4] .518	.061	.321
43	8.63	.392	[4] .038	.004	.673
45	8.70	.012	.064	[4] .158	[2] 3.764
46	8.69	.007	.362	.034	.577

[1] See table 2 for names of soils.
[2] Average of only 2 specimens.
[3] Some specimens not weighed because of stripped threads.
[4] Average of only 3 specimens.
[5] Only 1 specimen weighed.
[6] 2 sets of specimens removed.
[7] Specimens completely corroded away.
[8] Average of only 4 specimens.
[9] Average of 8 specimens.
[10] Specimens missing.

NOTE.—In soils 8, 23, 29, 33, and 39 the brass caps connected to the lead nipples experienced considerably more corrosion than caps attached to brass or iron nipples.

The losses of the galvanized nipples were severe in several soils. As the nipples were threaded at each end after being galvanized and as part of the threads were exposed, some of the corrosion loss is a loss of iron, rather than of zinc. However, in a few soils, much, if not all, of the zinc disappeared and in one location the nipples were so deteriorated that they broke when picked up. Since both iron and zinc corrode badly in this soil, the corrosion is not necessarily to be attributed to the attachment of the nipple to the brass cup.

2. COPPER AND COPPER-ALLOY PIPES AND RODS

Two years after the cast caps, referred to above, were buried, it was decided to test specimens of copper and brass pipe since, at that time, these materials were being advocated as substitutes for lead in water-service connections in city streets. It was not planned to inspect these specimens in 1932, but local conditions made it advisable

to remove sets of these specimens from three sites. The data obtained from these specimens are given in table 9. The depth of the pits was insufficient to justify measurement because of the low accuracy of the results obtainable.

TABLE 9.—*Corrosion of copper and copper-alloy pipes and rods*

[Losses in ounces per square foot per year]

Materials [1]	Soil no. 11 [2] 6.08 years		Soil no. 22 5.97 years		Soil no. 34 5.86 years	
	Loss	Condition	Loss	Condition	Loss	Condition
A	0.094	Pd [3]	0.286	Pd	0.218	Pd
N	.024	d	.067	d	.021	d
M	.026	P	.079	P	.032	P
P	.011	P	.085	P	.036	P
Me	.067		.208	d	.184	d
B	.062	Pd	.177	P	.113	Pd

[1] See table 2 for soil numbers.
[2] See table 1 for list of materials and Research Paper No. 359, page 590, for analyses.
[3] P = pitted; d = copper-colored discoloration, probably indicating dezincification or redeposition of spongy copper.

Dezincification, which weakens the materials, was evident on most of the alloy specimens. Specimens A, B, and Me, all of which contain approximately 40 percent of zinc, show the highest rates of loss.

3. LEAD CABLE SHEATH

Lead is frequently used underground for water services and sometimes lead-sheathed cables are placed in direct contact with the soil, although it is more common practice to draw the cables into ducts. Specimens of two kinds of lead obtained by flattening sections of cable sheath were buried in a considerable number of soils in 1922 and in other soils 2 years later. Table 10 shows the rates of corrosion found for the specimens removed in 1932. It will be noted from table 10 that the rates of loss of weight are considerably lower than for ferrous metals. The rate of penetration is also lower and in most soils it is negligible. In soil no. 1, the specimen of lead containing approximately 1 percent of antimony was punctured in several places as was the corresponding specimen removed in 1930. Since specimens in no other soil have been corroded at nearly the same rate, it appears that the pitting was the result of some peculiarity of the soil rather than of impurities in the metal. Although specimens were not punctured in any soil except soil no. 1, deep pits have been observed in specimens from several sites and it must be concluded that lead is attacked by some soils.

While table 10 and similar data reported in earlier papers apparently indicate somewhat higher rates of corrosion of specimens containing 1 percent of antimony, similar tests conducted on this material and on commercial lead by the Bell Telephone laboratories show no significant difference in the rates of corrosion of the two materials. Some of the Bell Telephone laboratory specimens were buried in the trenches used for the Bureau of Standards tests. Their specimens were much smaller, but more specimens were placed in each location.

TABLE 10.—*Corrosion of lead sheath*

Soil no.	Soil	Duration of test (years)	Spec. [1]	Loss, oz per sq ft per yr.	Penetration (mils per yr.)
1	Allis silt loam	9.60	A	0.203	12.4
			H	.147	9.7
3	Cecil clay loam	10.14	A	.072	.5
			H	.057	.5
8	Fargo clay loam	9.86	A	.103	2.8
			H	.031	1.6
13	Hanford very fine sandy loam	8.25			
14	Hempstead silt loam	9.88	A	.172	3.8
			H	.081	2.9
16	Kalmia fine sandy loam	10.02	A	.097	2.8
			H	.075	1.4
18	Knox silt loam	9.79	A	.118	3.7
			H	.033	1.5
19	Lindley silt loam	9.71	A	.178	2.5
			H	[2]	1.0
23	Merced silt loam	10.18	A	.057	.6
			H	.034	.5
28	Montezuma clay adobe	7.73	A	.129	4.0
			H	.105	1.8
32	Ontario loam	9.57	A	.085	.7
			H	.040	.5
33	Peat	9.66	A	.148	1.9
			H	.116	1.7
37	St. Johns fine sand	10.06	A	.100	1.0
			H	.100	1.5
39	Sassafras silt loam	9.89	A	.103	4.1
			H	.115	3.6
40	Sharkey clay	10.04	A	.280	2.8
			H	.168	1.8
42	Susquehanna clay	10.07	A	.061	1.6
			H	.058	.9
43	Tidal marsh	9.91	A	.039	.7
			H	.027	1.8
45	Unidentified alkali soil	9.85	A	.050	1.5
			H	.035	.5
46	Unidentified sandy loam	10.15	A	.075	1.9
			H	.028	2.1

[1] A contains approximately 1 percent of antimony; H, commercial lead.
[2] Eaten by gophers.

4. PARKWAY CABLE

For the transmission of small amounts of power underground, such as the lighting of street lamps, a combination of materials known as "parkway cable" is frequently used. This consists of 1 or more insulated wires surrounded by a lead sheath which is protected by a wrapping of fiber impregnated by a bitumen, 2 spiral wrappings of galvanized steel, and an outside wrapping of impregnated fibrous material. Table 11 shows the conditions of the various layers of the specimens removed in 1932.

TABLE 11.—*Condition of parkway cable*

Soil number [1]	Years buried	Outer fabric	Inner fabric	Outer [2] steel wrapper	Inner [2] steel wrapper	Lead sheath
1	9.60	F [3]	G	SR	G	W
3	8.13	B	G	P	SR	G
8	9.86	F	G	SR	G	G
13	10.18	BV	B	D	VBP	G
14	9.88	B	G	R	SR	G
16	8.06	B	G	BR	G	TW
18	9.79	F	G	G	G	TW
19	9.71	B	SR	G	G	W
22	9.65	F	G	SR	G	TW
28	7.73	D	G	BP	BR	G
32	8.63	F	G	G	G	TW
33	9.66	F	G	SR	G	TW
37	8.06	F	G	SR	SR	TW
42	8.08	F	G	P	SR	TW
43	9.91	F	G	R	G	G
45	9.85	F	G	R	SR	G
46	10.15	B	G	BR	SR	TW

[1] See table 2 for names of soils.
[2] All steel galvanized.
[3] Ratings: G, good; F, fair; B, bad; R, rusted; SR, slightly rusted; BR, badly rusted, TW, thin white corrosion product on lead sheath; W, white corrosion product on lead sheath; V, very; P, pitted; D destroyed. (Ratings by E. R. Shepard and I. A. Denison.)

5. MISCELLANEOUS METALS AND ALLOYS

About the time the Bureau of Standards started its study of soil corrosion, the United States Bureau of Mines started an investigation of metals suitable for use in mines. The Bureau of Standards was asked by the Bureau of Mines to bury certain specimens it had collected; and later, to avoid duplication of work, the Bureau of Standards undertook to report the results of its tests of these materials.

TABLE 12.—*Corrosion of miscellaneous metals and alloys*

[Average of 2 specimens]

Material [2]	Soil number [1]									
	13		29		42		43		45	
	Duration of test (years)									
	8.25		8.10		8.08		8.63		8.70	
	Loss [3]	Pits [4]	Loss	Pits	Loss	Pits	Loss	Pits	Loss	Pits
A	0.767	6.42	0.757	7.28	0.380	4.45	2.008	(5)	[6] 1.453	(5)
B	.050	0	.232	0	.011	0	.015	0	.097	0
C1	.013	1.70	.111	(5)	.010	0	.001	0	[6] .033	(7)
C2	.022	(7)	[6] .096	(5)	.008	1.60	.001	0	.034	3.56
C3				(5)	[6] .129	(5)	.004	0	[6] .145	(5)
H	.008	0	.144	.99	.017	0	.510	1.62	.024	.92
L	.023	0	.159	0	.026	0	.471	0	[6] .028	0
N	.118	0	.512	0	.118	0	.076	0	[6] .098	0
NN	.040	0	.314	0	.084	0	.049	0	[6] .043	0
P			[6] .506	3.70					[6] .302	(7)
S	.919	(5)	.763	(7)	.476	(7)	1.295	(7)	[6] 1.576	(5)
Z1	.333	5.94	.536	3.33	.056	.62	.176	(7)	[6] .995	(7)
Z2	.283	6.55	.549	4.93	.063	1.14	.242	8.11	[5] 1.027	12.8

[1] See table 2 for names of soils.
[2] See table 1 for names of materials.
[3] Loss in ounces per square foot per year.
[4] Average of deepest pit on each of 2 specimens in mils per year.
[5] Specimen partly destroyed.
[6] One specimen only.
[7] Holes through one or both specimens.

Table 12 gives the corrosion data on such Bureau of Mines specimens as were removed in 1932. These specimens are described briefly in table 1. As the specimens differed in thickness, comparison of specimens that were punctured is somewhat difficult. The condition of the aluminum specimens C1, C2, C3 was similar to that of those removed in the earlier periods and indicated the superiority of commercially pure aluminum and aluminum-manganese alloy such as material C2 over the duralumin type of alloys and the unsuitability of the latter for exposure to such conditions without adequate protective measures. There seems to be no significant difference in the behavior of the two varieties of lead N and NN. Although so far as is known to the Bureau of Standards, the two specimens Z1 and Z2 differ only in thickness, the thinner specimen Z1 corroded less in all soils in which the specimens were buried.

VI. CORROSION OF METALLIC PROTECTIVE COATINGS

1. GALVANIZED PIPE AND SHEET

A study of galvanized materials was started in 1924. It was hoped that several questions would be answered by the investigation. The major question, of course, was the action of soils on zinc and zinc iron-alloy. In addition, it was hoped that data could be obtained on the proper weight of zinc coating for different soil conditions. Information was also desired as to whether the nature of the ferrous metal beneath the zinc influenced the rate of corrosion. Perhaps the experiment would have been modified somewhat if the unavoidably wide spread of underground corrosion data had been realized or if the claims of the proponents of some of the galvanized materials had been more modest and less conflicting.

The precision of the data on the performance of galvanized materials underground is influenced not only by the variability of soil conditions, but by the difficulty of applying an exact amount of zinc and the still greater difficulty of distributing that zinc uniformly over the surface of the metal to be coated. If a large sheet of galvanized material is subdivided into sections of the size used in the experiment, a considerable variation in the weight of coating on the several sections may be expected. Consequently the failure of one kind of galvanized material prior to the failure of another kind carrying nominally the same weight of zinc may be due to differences in the actual weights of the coatings rather than to the differences in the base materials. The uncertainties on this account can only be overcome by using a large number of specimens and neglecting small apparent differences.

Table 13 gives the data on the pipe and sheet buried in all soils. The nominal weight of all coatings was 2 ounces per square foot, but the actual weight of the coatings departed considerably from this value. It will be seen that the rates of loss of weight and penetration are considerably less than the corresponding losses of the ferrous specimens, which indicates that zinc is more resistant to soil action than iron.

TABLE 13.—*Corrosion of galvanized pipe and 16-gage sheet*

Soil number[1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year				Rates of penetration in mils per year[6]				Condition[7]			
		A (pipe)[2]	A3[3]	B[4]	Y3[5]	A	A3	B	Y3	A	A3	B	Y3
1	8.62	0.332	0.350	0.396	0.403	.....	1.28	1.97	2.09	U	P	U	U
3	8.13	.038	.035	.034	.030	.....	.74	.62	.62	E	R	R	E
8	8.73	.057	.033	.032	.035	.....	.....	.....	.....	E	E	E	E
11	8.66	.048	.029	.051	.047	.....	2.42	2.89	3.23	R	P	P	P
13	8.25	.140	.207	.080	.238	.....	1.82	.61	1.82	E	P	R	U
14	8.76	.028	.014	.014	.015	.....	.....	.....	.....	E	E	E	E
16	8.06	.333	.106	.161	.095	.....	1.61	1.74	1.61	E	U	P	E
18	8.60	.029	.016	.015	.021	.....	.....	.....	.....	E	E	E	E
19	8.59	.069	.028	.040	.034	.....	.....	1.05	.....	E	E	R	R
20	8.62	.141	.146	.306	.104	.....	1.97	2.78	.81	R	P	P	U
22	7.97	.098	.....	.....	.....	.....	.....	.....	.....	R	.....	.....	.....
23	8.25	[8].945	.358	.260	.628	[8]6.67	3.58	2.12	4.00	P	P	P	P
28	7.73	[8].177	.463	.082	.066	.....	5.95	.91	.65	E	P	U	R
29	8.10	[8].484	.286	.554	.390	1.98	4.94	3.21	4.70	P	P	P	P
32	8.63	.037	.026	.020	.022	.....	.....	.....	.....	E	E	E	E
33	8.63	.171	.171	.213	.182	.....	1.85	1.97	1.62	U	P	P	P
37	8.06	.233	.338	.396	.....	.....	2.61	2.23	.....	R	P	P	P
39	8.51	.....	.113	.156	.107	.....	2.35	1.88	2.00	.....	P	P	P
40	8.09	.073	.....	.....	.....	.....	.....	.....	.....	E	.....	.....	.....
42	8.08	[8].036	.028	.027	.029	.....	.....	.....	.....	E	E	R	E
43	8.63	[8].114	.068	.155	.100	.....	.81	3.82	.68	E	U	P	U
45	8.70	[8].284	.057	.302	.078	.....	1.03	4.95	.69	U	U	P	U
46	8.69	.048	.008	.005	.007	.....	.....	.....	.....	E	E	E	E

[1] See table 2 for names of soils.
[2] A=pure open-hearth iron pipe. Coating=282 ounces per square foot.
[3] A3=pure open-hearth iron sheet. Coating=198 ounces per square foot.
[4] B=Bessemer steel sheet. Coating=162 ounces per square foot.
[5] Y3=Open-hearth steel sheet, 0.2 percent copper. Coating=2.15 ounces per square foot.
[6] Maximum penetration obtained by averaging deepest pit on each side of sheet.
[7] Symbols: U=uniformly corroded.
E=excellent.
R=rusted.
P=pitted.
[8] Average of 2 specimens.
[9] Average of 3 specimens.

Although the 3 varieties of base materials were selected in order to determine whether one was preferable to another for galvanizing purposes, the table answers the question only in a negative way. So far as can be determined from the data there is no significant difference in the corrosion resisting properties of the three kinds of specimens. Such differences as are apparent can be accounted for by variations in soil conditions or in the weight of the coatings. If table 13 is compared with the corresponding data for the 6-year period as shown in table 11 of Research Paper 359, it will be found that there is little definite evidence of an increased rate of corrosion of the older specimens. This indicates that the corrosion is still controlled by the zinc coating, although in many test localities this coating has been punctured. The letters in the last 4 columns of table 13 indicate the condition of the specimens. These columns are perhaps the most valuable part of the table, since no satisfactory way has been found to remove rust from the plates without removing zinc also and deviations of the surface of the plates from perfect planes made accurate pit measurements impossible.

TABLE 14.—*Effect of weight of zinc coating on rates of corrosion*

RATES OF LOSS OF WEIGHT

[In ounces per square foot per year]

Soil number [1]	Duration of test (years)	Galvanized pipe			Galvanized sheet [2]							18-gage			Black sheet [2] 18-gage		
		16-gage															
		A [2,3]	D [4]	Y [3]	A [3]	A [3]	A [4]	Y [3]	Y [3]	Y [4]	Y [3]	CA	CB	CY	CA-B	CB-B	CY-B
		2.82	3.48	3.47	1.79	1.98	2.65	1.57	2.15	2.76	2.92	1.87	1.66	2.16	0	0	0
13	8.25	0.140	0.196	0.154	0.229	0.207	0.167	0.433	0.238	0.152	0.207	0.101	0.092	0.089	0.941	0.822	0.905
28	7.73	.177	.203	.163	.760	.463	.683	.307	.066	.174	.082	.054	.093	.072	X	X	X
29	8.10	.484	.383	.391	.440	.386	.372	.397	.390	.345	.331	.447	.522	.421	1.26	1.105	1.087
42	8.08	.036	.036	.033	.027	.028	.028	.040	.029	.031	.028	.027	.028	.031	.497	.532	.492
43	8.63	.114	.172	.136	.099	.068	.062	.075	.100	.053	.065	.039	.057	.056	.723	.746	.410
45	8.70	2.84	.318	.225	.826	.057	.063	1.125	.078	.076	.065	1.037	.695	.495	X	X	X
RATES OF MAXIMUM PENETRATION [5] [In mils per year]																	
13					2.42	1.82	1.45	3.88	1.82	0.73	0.85	2.12	0.61	0.85	6.06	6.06	6.06
28					6.47	5.95	7.76	4.40	.65	1.55	.65	.65	.91	.65	X	X	X
29		1.98			4.57	4.94	4.11	4.38	4.70	1.67	2.65	4.69	3.02	3.64	6.17	6.17	6.17
42					.62	.62	.62	2.78	.62	.62	.62	.62	.62	.62	6.19	6.19	6.19
43					2.03	.81	.58	.70	.58	.58	.58	.58	.58	.81	5.79	5.79	4.40
45					7.13	1.03	1.26	6.90	.69	.57	.80	5.75	5.75	4.14	X	X	X
CONDITION OF SPECIMENS																	
13		E	E	E,R	P	P	U	P	U	U	U	P	P	U	H	H	H
28		E	E	E	P	P	H	P	R	U	R	U	U	U	H	H	H
29		U,P	U	U	P	P	P	P	P	U	P	P	P	P	H	H	H
42		E	E	E	R	E	E	P	E	E	E	E	E	E	H	H	H
43		E	E	E	P	U	E	U	U	E	R	E	R	H	H	H	P
45		R,U	E	R	H	U	U	H	U	U	U	H	H	H	X	X	X

[1] See table 2 for names of soils.

[2] Symbols: A, pure open-hearth iron.
B, Bessemer steel (when separated from another letter by a dash denotes sheets not galvanized).
C, 18-gage metal.
D, wrought-iron pipe.
Y, open-hearth steel containing 0.2 percent copper.
X, destroyed.
E, excellent.
H, holes.
P, pitted.
R, rusted.
U, uniformly corroded.

[3] 2 specimens in each soil.

[4] 1 specimen in each soil.

[5] Weight of coating in ounces per square foot.

[6] Maximum obtained by averaging deepest pit on each side of sheet.

2. RELATION OF WEIGHT OF ZINC COATING TO CORROSION

In addition to the galvanized pipe and sheet described above, specimens of pipe and sheet having other weights of coating were removed from six soils and the results of their examinations are given in table 14, in which are repeated some of the data of table 13. It will be seen that, in general, the specimens carrying the heaviest coatings resisted soil action best, but there are a number of exceptions to this rule.

In the last three columns are given data on specimens of materials which were not galvanized in order that the effects of the zinc may be seen more readily.

3. LEAD-COATED PIPE

Since lead corrodes more slowly than iron under most soil conditions, it was thought that lead-coated pipe might be satisfactory for underground use. Specimens of lead-coated pipe were buried at some test sites in 1922 and at others in 1924. Data on specimens of this kind removed in 1932 are given in table 15. The thickness of the coating is about 0.002 of an inch and as might be anticipated from a study of the data on the lead cable sheaths, the coating was punctured in a large number of the soils.

TABLE 15.—*Corrosion of lead-coated steel pipe*

Soil number [1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year [2]	Rates of maximum penetration in mils per year [2]	Soil number [1]	Duration of test (years)	Rate of loss of weight in ounces per square foot per year [2]	Rates of maximum penetration in mils per year [2]
1	8.62	0.438	10.4	28	7.73	0.126	8.7
3	8.13	.075	5.9	29	8.10	.640	7.0
8	8.73	.073	9.4	32	8.63	.074	5.6
11	8.66	.097	4.4	33	8.63	[4] .475	[4] 7.0
13	8.25	.051	5.3	37	8.06	.240	6.5
14	8.76	.029	4.3	39	8.51	.087	7.3
16	8.06	.172	6.1	40	8.09	.134	6.5
18	8.60	.036	7.0	42	8.08	.063	2.8
20	8.62	.230	6.3	43	8.63	.238	10.3
23	8.25	[3] .149	[3] 10.1	45	8.70	.195	8.5
				46	8.69	.036	3.4

[1] See table 2 for names of soils.
[2] Average of 2 specimens except as otherwise noted.
[3] Average of 4 specimens.
[4] 1 specimen only.

If the depths of pits on the lead-coated specimens are compared with the depths of the pits on uncoated steel pipe in the same soils for the same periods of exposure, it will be found that in some soils the pitting on the coated specimens is the deeper and in other soils the shallower. The differences in the rate of pitting between the coated and bare pipe are not great and may be attributed to accidental conditions. There is little definite evidence indicating that the pitting was accelerated by the difference of potential between iron and lead.

TABLE 16.—*Corrosion of calorized specimens*

Soil number [1]	Duration of test (years)	Rates [2] of loss of weight in ounces per square foot per year		Rates [2] of maximum penetration in mils per year	
		Dry calorized	Wet calorized	Dry calorized	Wet calorized
13	8.25	0.214	0.082	3.36	4.33
28	7.73	.310	----------	5.66	----------
29	8.10	.376	.335	4.50	7.01
42	8.08	.174	.077	5.07	6.32
43	8.63	.800	.820	3.22	4.22
45	8.70	.496	.260	5.69	5.17

[1] See table 2 for names of oils.
[2] Average of 2 specimens.

4. CALORIZED PIPE

Specimens of calorized steel pipe prepared by two processes were buried in seven soils in 1924. Table 16 gives the results of the examination of the calorized specimens removed in 1932. The data indicate that the treatment of the specimens reduced the rates of corrosion materially but did not afford complete protection against soil action. It should be noted that all of the soils from which calorized specimens were removed are above the average in corrosiveness with respect to ferrous materials.

5. SHERARDIZED AND LEAD-COATED BOLTS

At the request of the corrosion committee of the American Foundrymen's Association, which was interested in bolts for pipe flanges and fittings used underground, specimens of sherardized, lead-coated, and wrought-iron bolts and nuts were buried in six corrosive soils.

Table 17 shows the rates of loss of weight of the specimens removed in 1932. Both treatments of the bolts increased their resistance to corrosion. It is doubtful whether the differences between the rates of loss of weight for the sherardized and lead-coated bolts are significant.

TABLE 17.—*Rates of loss of weight of bolts and nuts*

[Average of 4 specimens in ounces per square foot per year]

Soil number [1]	Duration of test (years)	Bolts			Nuts		
		G [2]	D	F	G	D	F
13	8.25	0.247	1.252	0.267	0.255	1.132	0.251
28 [3]	7.73	.604	2.901	----------	.755	2.573	----------
29	8.10	.647	1.132	.881	.361	1.242	.752
42	8.08	.193	.592	.194	.171	.402	.188
43	8.63	.922	1.564	.499	.528	.925	.409
45	8.70	.615	1.479	.526	.400	1.724	.433

[1] See table 2 for names of soils.
[2] D=wrought iron; F=lead-coated; G=sherardized.
[3] One specimen only.

VII. CONCLUSION

The data presented in this report are for the more corrosive soils in the investigation and do not represent the average corrosiveness of all soils.

The data are in substantial agreement with those presented in earlier reports and support the conclusions already reached.

There are indications that the rate of corrosion decreases with time in most soils because of more stable trench conditions or the formation of corrosion products. The rate of decrease in general diminishes with time, indicating that a fixed rate of corrosion may ultimately be reached.

On account of unavoidable variations in soils of the same type, in metals even of the same kind, and in methods of construction, exact rates of corrosion cannot be predicted, but approximate rates of corrosion can be given for specified metals and soil conditions.

Differences in the rate of penetration of different pipe-line materials by soil action in the same soil are much smaller than differences in the rate of penetration of the same material in different soils. The type of soil rather than the variety of ferrous material is usually the controlling factor with respect to corrosion. In certain soils, however, one type of material may corrode much more rapidly than some other material and for this reason the soil to which it is to be exposed should be considered in selecting material for a pipe line.

The maximum rate of corrosion on a pipe line may be greater than the rate given in this report for the same material and soil because of the greater exposed area and local adverse conditions. Lower rates of corrosion over the same period of exposure are not to be expected.

Additional correlations between rates of corrosion and soil types should make the soil survey maps and reports of the United States Department of Agriculture of great value in preliminary estimations of soil corrosivity in territories where new lines are to be laid.

Copper, and alloys high in copper, corrode less rapidly than most ferrous materials in the soils investigated.

A zinc coating weighing 1 ounce per square foot of exposed surface should extend the life of the coated material at least 6 years in very corrosive soils and much longer under more favorable conditions.

This report is the joint product of nearly all of the members of the underground corrosion section of the Bureau. R. H. Taylor and Robert B. Hobbs are responsible for the supervision of the cleaning of the specimens and the determination of losses of weight and pit depths. All of the calculations were made or checked by E. R. Shepard. Both he and I. A. Denison have taken an active part in determining the significance of the data, as have those mentioned earlier, though to a less extent. Suggestions have also been received from other members of the section and from cooperating manufacturers and public-utility associations.

APPENDIX 1. ERRATA IN EARLIER PUBLICATIONS

Although each step in the determination of the data has been taken independently by two persons and considerable care has been exercised in the transfer of data from one stage of production to the next, errors have crept into all of the reports on the underground-corrosion investigation. None of the errors so far discovered affect the general conclusions which have been reached and most of them are within the limits of the errors of the experiments. There are a few, however, which interfere somewhat with the comparison of data from year to year or with the comparison of materials in certain soils.

Below are tabulated all the errors so far discovered in the earlier publications on underground corrosion which appear to be of any importance.

Notices of errors or omissions in the present report or in the earlier ones will be appreciated.

Technologic Paper No. 368.

Page 451, change "Nugent Steel Castings Co." to read "Sivier Steel Castings Co."

Page 454, under E, Muntz metal, change "¾ inch" to read "½-inch I.P.S."

Page 454, under F, Copper steel tube, change "15 percent" to read "1.5 percent."

Page 530, under list of organizations include "The Barrett Co.—C. S. Reeve."

Research Paper No. 329.

Page 12, table 7, under copper bearing steel, soil 29, change "2.01" to read "1.98."

Page 13, table 8, under pure open-hearth iron, soil 23, change "27" to read "18"; under sand mold cast iron, soil 23, change "51" to read "35".

Page 21, table 16, under a, Soil 23, change "27" to read "23.6"; tables 17 and 18, footnote 1, change "table 8" to read "table 5"; tables 11 to 16, footnote 1. Change "table 4" to read "table 5."

Page 23, table 18, under a, soil 23, change "2.4" to read "24," for soil 40, make the following changes: under B, "11.1" to read "8.2"; K, "14.9" to read "11.9"; M, "14.4" to read "11.5"; Y, "13.3" to read "10.3"; L, "12.7" to read "8.2"; Z, "13.6" to read "9.7".

Page 25, table 20, under a, soil 23, change "23.6" to read "25".

Page 26, table 21, under rates of Penetration for 8 years, soil 23, change "21.7" to read "20.7".

Page 33, table 23, under I, soil 45, change "1.137" to read "1.297".

Page 34, table 25, under Age of Specimens, soil 120, change "1.95" to read "1.97", and for soil 121, change "1.97" to read "1.95".

Research Paper No. 359.

Page 593, table 7, under Description, for D, F, and G, change "2" to read "3.5" after bolts.

Page 598, table 11, for soil 1, under A3, change "7.993" to read "0.7993"; under B change "6.627" to read "0.6627"; under Y3 change "6.769" to read "0.6769".

Page 604, table 17, in footnote change "D" to read "K", "K" to read "D", "M" to read "P", "P" to read "M".

WASHINGTON, August 9, 1933.

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